

UNCLASSIFIED

AD 297 130

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CATALOGED BY ASTIA
AS AD NO. 297130

63-2-5

GENERAL ENGINEERING LABORATORY

Qualified requesters may
obtain copies of this
report from ASTIA.

DEVELOPMENT OF INORGANIC BINDERS

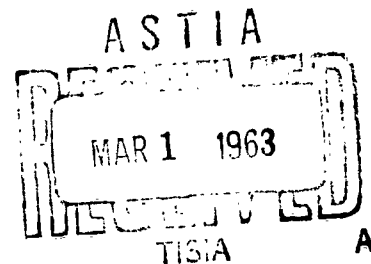
October 27, 1960

Prepared Under Navy,
Bureau of Aeronautics

Contract Noas58-850c

Final Report

June 27, 1958 through September 30, 1960



GENERAL  ELECTRIC

The information contained in this report has been prepared for use by the General Electric Company and its employees. No distribution should be made outside the Company except when indicated below:

DEVELOPMENT OF INORGANIC BINDERS

October 27, 1960

Prepared Under Navy,
Bureau of Aeronautics

Contract NOas58-850c

Final Report

Covering Work Done

June 27, 1958 through September 30, 1960

Project Leader Henry T. Plant

Associates R. T. Girard
 G. A. Rice
 H. R. Wisely

Project Consultant K. N. Mathes

Project Manager T. J. Jordan

General Engineering Laboratory
General Electric Company
Schenectady, New York

Report Submitted by: Insulating Materials Department
General Electric Company
Schenectady, New York

TABLE OF CONTENTS

	Page
Project Aims	i
Accomplishments	ii
Conclusions and Recommendations	iii
 EXPERIMENTAL RESULTS	
Introduction	1
Continuous Filament Reinforcing Fibers for High Temperature Laminates	4
Fused SiO ₂ Yarn Strength	6
SiO ₂ Yarn Treatment	8
Effect of Bonding Compositions on SiO ₂ Yarn	9
Protective Yarn Encapsulation	13
Fiber Status	15
Inorganic Bonding Materials for High Temperature Laminates	17
Phosphate Binders	18
Aluminum Phosphate Bonded Cements	21
Effect of Heat on Strength of Formulation 3 - Bonded Laminates	24
Modifications of Cement Formulation 3	32
Asbestos in Aluminum Phosphate Cements	33
Laminates Bonded with Pre-reacted Phosphate Adhesives	34
Colloidal Binders, Extensible Binders, Low Temperature Glass Binder	35
Laminate Fabrication by Hot Pressing	37
Techniques Used in Fabricating Cement Bonded Laminate Samples	39
Cement Preparation	39
Filament Wound Samples	39
Wet Lay-Up Fabrication	42

TABLE OF CONTENTS (continued)

	Page
Physical Properties of SiO ₂ Fiber Reinforced Aluminum Phosphate Bonded Laminates	44
Flexural Strength and Elastic Modulus	44
Impact Strength	45
Moisture Absorption	45
Thermal Shock Resistance	46
Electrical Properties	46
Status of Inorganic Cement Bonded Laminates	48
Results	48
Mechanisms Effecting Laminate Strength	48
Means for Future Improvement of Laminate Strength	49

TABLE OF CONTENTS (continued)

	Page
Physical Properties of SiO ₂ Fiber Reinforced Aluminum Phosphate Bonded Laminates	44
Flexural Strength and Elastic Modulus	44
Impact Strength	45
Moisture Absorption	45
Thermal Shock Resistance	46
Electrical Properties	46
Status of Inorganic Cement Bonded Laminates	48
Results	48
Mechanisms Effecting Laminate Strength	48
Means for Future Improvement of Laminate Strength	49

TABLES

	Page
I. Effect of Desizing and Substitution of High Temperature Lubricant on the Tensile Strength of 150 4/3 SiO ₂ Yarn.	7a
II. Effect of Bonding Agents on the Tensile Strength of SiO ₂ Yarn (150 4/3)	10a
III. Representative Flexural Strength (psi) of Filament Wound Laminates Bonded with Cement Formulation 3.	24a
IV. Representative Cement Compositions Used in Laminate Fabrication and Flexural Strength of Resulting Laminates.	31a 31b
V. Flexural Strength and Elastic Moduli of Several Cement Bonded Laminates	44a
VI. Summary of Physical and Electrical Properties of Some Inorganic Laminates	47a 47b

TABLE OF FIGURES

	Page
1. Stress Strain Curves for Laminate Components	a-1
2. Filament Winding Mold	38a
3. Filament Winding Procedure.	39a
4. Mold for Reinforced Ceramic Air Foil.	42a

PROJECT AIMS

Development of an inorganic binder for use as a matrix with glass fibers (or other high temperature, non-metallic, inorganic fiber reinforcement) thus making possible the fabrication of a non-metallic structural laminate that does not deteriorate significantly upon exposure to temperatures in the -65 to 1200 F range (-54 to 650 C).

The development effort was aimed primarily toward achieving the following target objectives which are based on high temperature radome requirements:

- a. The laminate shall have minimum notch sensitivity and shall not be subject to brittle failure.
- b. The ultimate flexural strength of the laminate (inorganic binder reinforced with high temperature fibers) shall be at least 40,000 psi after exposure for 1/2 hour at 1200 F (650 C).
- c. The laminate shall exhibit no loss in strength after 24 hours immersion in water at room temperature. The increase in dielectric constant and loss tangent as a result of immersion shall not exceed 10% and 30% respectively.
- d. The dielectric constant of the laminate shall not be greater than 5.0 at 10,000 megacycles in the as received condition and shall remain essentially unchanged over a temperature range to 1200 F. The loss tangent over this temperature range shall not exceed 0.010.
- e. The specific gravity of the binder shall not exceed 3.0.
- f. Techniques for fabricating the completely inorganic laminate shall depart from present methods used in forming reinforced plastic laminates to the minimum extent possible, particularly insofar as temperature of fabrication is concerned.

ACCOMPLISHMENTS

Fused silica fiber was selected as the best currently available high temperature continuous filament for laminate structures. Aluminum phosphate bonded cements were found to be consistently superior to other materials tested as matrices in fiber reinforced laminate samples. Particularly good laminate strengths were obtained when asbestos microfibers were included as a portion of the filler content in the cementing matrix.

Filament wound laminate specimens (fused silica yarn or roving, bonded with asbestos and zircon filled aluminum phosphate cement, cured at 300 C. after drying at 150 C) were characterized by:

- a. Unusual flexibility, for a non-metallic inorganic material, and virtual absence of notch sensitivity on impact. Brittle failure of the bonding cement in flexure frequently left the sample apparently unbroken because the reinforcing fibers remained intact.
- b. Average flexural strength of laminate samples formed with pre-tensioned reinforcement was 29,000 psi when measured at room temperature, 24,000 psi when measured at 500 C after 1/2 hour at temperature. Samples formed without pretensioning averaged 20,000 psi at room temperature and 24,000 psi at 500 C after 1/2 hour at temperature. When tested at room temperature after having been heated at 500 C the strength was lower.
- c. Laminate structures appeared unharmed by immersion in water. The moisture absorbed (12 to 18%) was readily removed by drying and caused no permanent change in electrical properties.
- d. Dielectric constant of the dry laminate was in the 2.8 to 3.0 range (9,150 M/sec.) and did not change significantly with temperature. Loss tangent tended to be erratic in those laminates containing asbestos. When alumina replaced asbestos as the cement filler, the loss tangent measured at 9,150 M/sec. was 0.012, remaining essentially constant over the temperature range from 20 to 600 C.
- e. Bulk density of the porous laminate ranged from 1.6 to 1.8 gm/cc. The specific gravity of a void-free laminate having this general composition probably would lie between 2.5 and 2.8 gm/cc.
- f. Exceptional ease of fabrication is perhaps the most outstanding characteristic of these laminate compositions. Because of the aluminum phosphate adhesive used, simple evaporation of water from the cement slurry produces a strongly bonded structure that can be removed from the forming mandrel for curing at 300 C. When thoroughly heated at this low temperature the cement becomes permanently "set".

CONCLUSIONS AND RECOMMENDATIONS

The laminate described is suitable for certain limited high temperature applications but, in its present state of development, lacks a number of desirable characteristics. The experience gained in working with this novel combination of materials has provided a basis for further progress and has specified the problem areas requiring intensive developmental effort.

Even the strongest of our inorganic laminate samples utilize very little of the inherent strength of the reinforcing fiber because of the relatively slight extensibility of the crystalline bonding matrix. A small increase in bond extensibility would notably increase laminate strength. A distinct but less dramatic improvement would accrue from a decrease in voids within the bond.

The prevalent loss of strength now observed, when laminates are tested at room temperature after having been subjected to high temperature, we believe derives from the differential thermal expansion of bonding cement and fused silica reinforcing fiber; along with the slow annealing of the fiber which is placed in tension at elevated temperatures. Modification of the aluminum phosphate adhesive bond and change in cement filler content to provide a thermal expansion more nearly approaching that of fused silica should prove advantageous. Further advances in laminate strength may also be realized when reinforcing fibers having higher elastic moduli and annealing temperatures become available.

Loss of fiber integrity and consequent embrittlement of the reinforcing fibers due to inter-fiber sintering at high temperature is one of the problems requiring attention. Modification of the aluminum phosphate adhesive to suppress its reactivity with the fused silica fiber reinforcement, and development of a suitable protective film for the continuous filament reinforcement, are

two approaches that have been tried with some degree of success. Further effort in this area is required.

We are convinced that the full capabilities of reinforced inorganic laminates have scarcely been tapped. Their potential worth as strong, easily fabricated, temperature resistant, structures strongly recommends that further effort be directed toward the continued development of this youngest member of the laminate family.

EXPERIMENTAL RESULTS

STRESS STRAIN CURVES FOR LAMINATE COMPONENTS

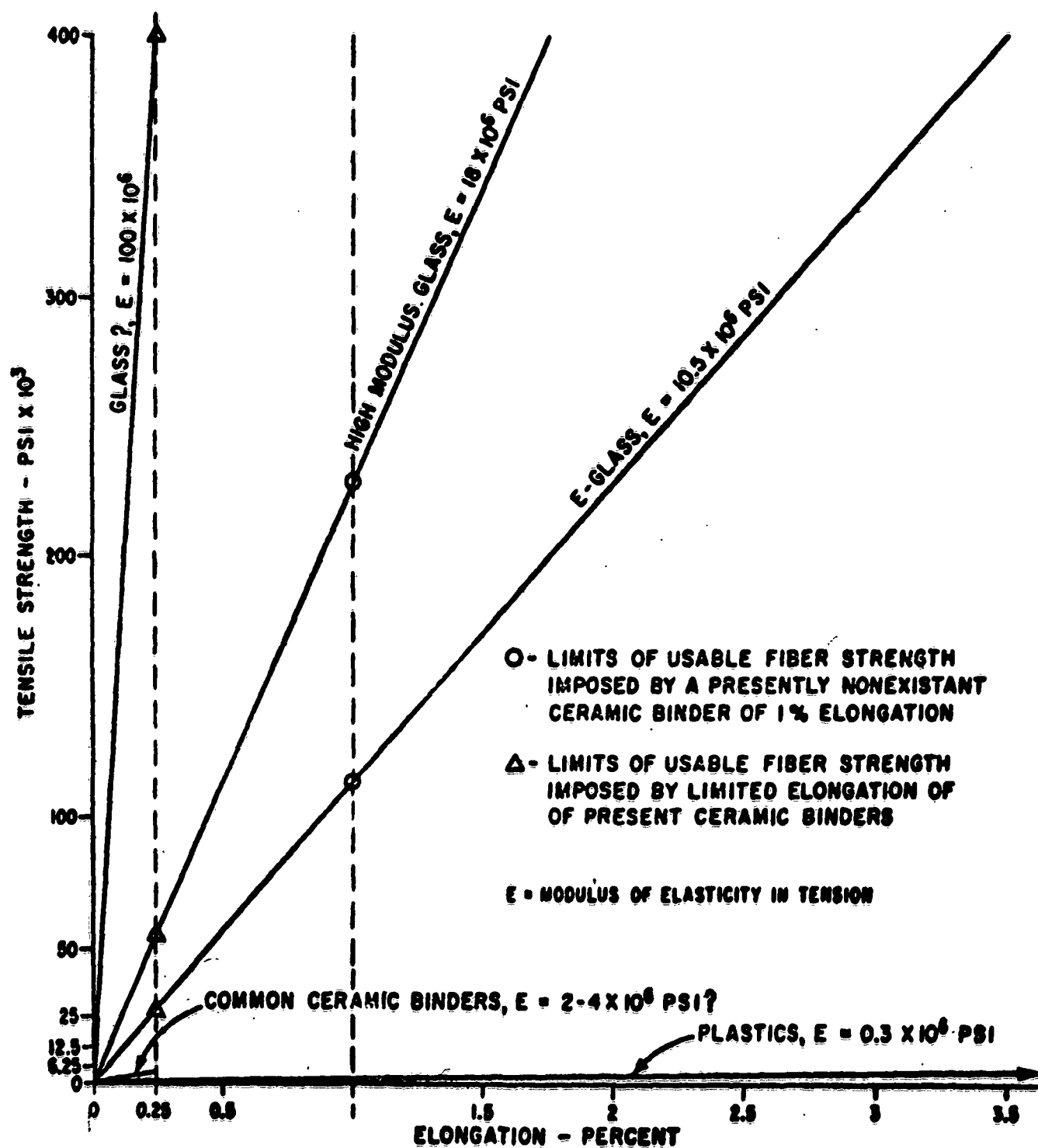


Figure 1

INTRODUCTION

Fiber reinforced inorganic laminates are, inevitably, complex composite structures. The physical properties of such composites are governed by the physical and chemical interaction of the several component phases. For this reason it is difficult, if not impossible, to truly isolate one phase from another for purposes of experiment or discussion. Convenience in presenting the experimental results has dictated an artificial segregation, but it will soon be noted that an understanding of the behavior and contribution of any one phase in the laminate structure requires a consideration of effects due to many other factors.

Although there is a superficial similarity between fiber reinforced plastic and fiber reinforced inorganic laminates, in the present state of the art, they are fundamentally quite dissimilar. The situation is pictorialized in Figure 1 which presents a simplified and idealized version of the strength capabilities of laminate systems. For the sake of demonstration we have assumed laminates constructed from equal volumes of binder and reinforcing fiber, so that a load applied to the laminate is distributed between binder and reinforcement in proportion to their respective elastic moduli. The reported tensile strength of 400,000 psi with 3.5% elongation is shown for "E" glass, though in practical use the realized values may be no more than half of these. Our assumption that inorganic binders may elongate by 0.25% before rupturing is in the realm of wishful thinking. But despite assumptions and approximations, the diagram does clearly show (as more fully discussed in Report IV pp. 12a-14) the material requirements that are needed to produce high strength laminates.

As demonstrated in Figure 1, the phenomenal strength displayed by fiber reinforced plastic laminates is attributable to the ability of the low modulus

plastic matrix to stretch sufficiently when loaded to allow the relatively high modulus glass reinforcing fibers to assume their maximum burden. On the other hand, glass fiber reinforced laminates bonded by inorganic cements (with their normally high modulus, low strength and low extensibility) cannot take advantage of more than about 25,000 psi of the possible 400,000 psi strength of the reinforcing fibers because of bond failure due to limited extensibility.

Clearly, there are two means for obtaining higher laminate strengths:

1. Use a more extensible binder so that a larger portion of the strength of the reinforcing fibers can be utilized. A ceramic binder capable of only 1% extension would allow 100,000 psi to be assumed by the fiber.
2. Use a higher modulus fiber so that more fiber loading occurs before the extension limit of the binder is exceeded. A reinforcement having twice the 12×10^6 psi modulus of "E" glass would, in effect, double the available strength of the fiber. Using the present binder, it would be possible to realize the total strength of the reinforcing fiber if the fiber had an elastic modulus in the 100×10^6 psi range. Development of this wonder fiber is not likely to be accomplished in the near future.

Two less obvious methods for improving laminate strengths are also indicated:

1. Modification of the binder to produce controlled micro-cracking thus "fooling" it into a greater extensibility without complete rupture.
2. Pre-stressing the fiber reinforcement in tension. This places the binder under a compressive stress which must be overcome by extension of the loaded fiber before any extension of the bond occurs.

One other feature that differentiates plastic-bonded from inorganic cement-bonded laminates lies in the interaction between the bonding matrix

EXPERIMENTAL RESULTS

and the reinforcing fibers. In the plastic bonded system the reinforcing fibers are able to act independently of each other not only because of the elastic quality of the encapsulating plastic but also because a physical, rather than chemical, bond between glass and plastic allows a slight amount of stress-equalizing slippage. In contrast, an inorganic cementing matrix fails by cracking and these cracks serve as stress risers in the laminate structure. Crack propagation from the brittle matrix through the fibers is aggravated by strong inter-fiber bonding that is probably chemical in nature.

Thus we see that a many faceted approach is required for the actual development of a high strength inorganic bonded laminate structure. First we require a fiber reinforcement having the highest possible elastic modulus and tensile strength. Next we must make every effort to retain these properties when the fibers are imbedded in an inorganic bonding cement. Ideally, the bonding cement should be capable of an extension approaching that of the fiber reinforcement. Lacking this, the cement bond must have an elastic modulus exceeding 10^6 psi and the highest possible extensibility.

CONTINUOUS FILAMENT REINFORCING FIBERS FOR HIGH TEMPERATURE LAMINATES

Any fiber intended for use as the reinforcement in a high temperature (1200 F) laminate structure must, obviously, have a high tensile strength at both low and high temperatures.

Probable lack of high temperature strength excluded "E" glass fiber (so widely used in reinforced plastics) from serious consideration as high temperature reinforcement, but its ready availability made it a convenient material for use in many tests. Inorganic bonded "E" glass filament wound laminate samples tested in flexure failed by plastic flow in the 600 - 700 C (1100 - 1300 F) region and doubtless would exhibit creep at much lower temperatures. (See Report VIII, pp. 12-14)

The more refractory Refrasil fiber (from H. I. Thompson Glass Prod., a 96% SiO₂ glass made by chemical leaching of "E" glass cloth or yarn) had poor initial strength, less than 1/10 that of the parent "E" glass. Preliminary tests indicated that the strength of this material could be improved to some extent by heat treatment. (See Report I, pp. 10-16) A similar high silica content glass fiber (obtainable in experimental quantity from Owens-Corning Fiberglas Co.) is reported to have low initial strength also and, consequently was not included in our investigation.

Some high silica content glass fibers were drawn from a rod of Vycor in the General Engineering Laboratory. Their room temperature tensile strength was found to be similar to that of comparably handled pure silica glass fibers and their service temperature limit was estimated to be 1800 F (980 C). If made available in commercial quantities, such fibers might be applicable as high temperature reinforcing filaments. (See Reports IV, pp. 37-38, and VI, pp. 17-18)

Due to production difficulties, Houze Glass Co. was unable to supply us

with experimental quantities of the high temperature, high modulus, aluminum-silicate fiber being developed by them. Hand drawn fibers are said to show an elastic modulus as high as 49×10^6 psi and tensile strength in excess of 1,000,000 psi. However, the fiber is reportedly prone to mechanical degradation; a slight mechanical shock not only reduces the tensile strength but also reduces the modulus of elasticity. (See Reports II, p. 7, and VI, pp. 16-17)

The high modulus (16 to 18×10^6 psi) beryllia-containing glass fiber, made by Owens Corning Fiberglas Corp. for Wright Air Development Center, is reported to have a service temperature limit somewhat less than that of "E" glass. Therefore, this fiber is unsuitable as a high temperature reinforcement. However, several inorganic bonded filament wound laminate samples were fabricated from this high modulus glass fiber, which was obtained as 200 filament roving with a silane finish. The results of room temperature flexural tests on these specimens were quite disappointing since the strength was about half that obtained with roughly comparable silica glass reinforced laminates. Fabricating difficulties in handling the delicate roving and probable sensitivity of the high modulus glass to mechanical damage undoubtedly contributed to the poor strengths observed. (See Report VII, pp. 34-35) That the lower strength was not directly caused by the higher modulus of the fiber but occurred in spite of it, may be judged from the several tests made on laminate samples reinforced with asbestos yarn having a core of Monel wire (elastic modulus 26×10^6 psi) or a core of fiber glass (elastic modulus 12×10^6 psi). Here a notable 50% improvement in laminate strength accompanied the use of the higher modulus reinforcement. (See Report VII, pp. 32-34)

High purity fused silica fibers drawn from quartz glass appeared to be the only high strength, high temperature continuous filament reinforcement

presently available in commercial quantity. Initially we were able to obtain this material from the G. E. Lamp Glass Dept., Cleveland, Ohio, as starch-oil coated fibers in the form of 150 4/3 yarn. The largest proportion of the work done on this project involved the study of these fused SiO_2 fibers in the form of 150 4/3 yarn as laminate reinforcement. SiO_2 fibers later became available as 12 end roving and woven cloth.

FUSED SiO_2 YARN STRENGTH

Individually tested fused SiO_2 fibers are reported to have phenomenally high tensile strength, providing that they are tested in their pristine "as drawn" condition. Such strength is not to be expected from yarn strands composed of fibers which have undergone a starch-oil coating treatment, twisting, and handling in uncontrolled atmospheres. What, then, is the practical strength of a 2400 filament strand of this 150 4/3 fused SiO_2 yarn? And how is this strength affected by subsequent treatment that the yarn receives when incorporated as reinforcement in a laminate structure? To answer these questions, a simple tensile test was used (See Reports III, p. 11, and IV, p. 18) in which a 2400 filament strand of the yarn was loaded at the approximate rate of 3,500 gms/min. until broken. The observed breaking loads provided comparative values of yarn strength following various treatments.

The tensile load required to break the 150 4/3 SiO_2 yarn "as received" varied somewhat from spool to spool and more greatly from batch to batch, reflecting probable variation in production conditions and changes in relative humidity of the atmosphere in which the samples were tested. Breaking loads ranged from 10 to 16 Kgms. We were not surprised to note that yarn heated at 90°, 125°, or 200°C to drive off moisture always displayed increased tensile strength (in the 12 to 26 Kgm. range). Nor was it unusual to find that yarn tested after exposure to, or immersion in, water invariably broke with lower

loads (6 to 10 Kgm). Silicate glasses are notoriously sensitive to moisture attack, particularly when stressed; a characteristic that is shared by pure SiO_2 . Strength lost because of moisture attack on the stressed yarn was almost completely recovered if the yarn strand was thoroughly dried before testing. (See Reports III p 12; IV p 19; V p 27; VI p 20; and VII p 48)

But how strong was this yarn at elevated temperatures? We were dismayed to find that a strand of the SiO_2 yarn "as received" had a negligible tensile strength following exposure to 500 C. Burning off of the starch-oil binder, which had provided low temperature lubrication between fibers, accounted for a certain loss in strength attributable to abrasion damage. But heat treated yarn, if relubricated with motor oil, regained only one third of its original dried strength. Some irreparable damage seemed to have occurred.

Yarn samples before and after heating at 500 C for 16 hours gave identical X-ray powder-diffraction patterns. Thus, no detectable devitrification of the glass had developed as a result of the extended heat treatment.

We were fortunate in being able to obtain some very revealing electron micrographs of the starch-oil coated SiO_2 fibers before and after heating. These were compared with micrographs of uncoated, hand-drawn, SiO_2 fibers (before and after heat treatment) and silane-coated "E" glass fibers, similarly heated at 500 C. The uncoated SiO_2 fibers appeared to have "withered" slightly when heated. The silane coated "E" glass displayed a somewhat pitted surface with a shallow area that had apparently "scaled off" after firing. But these surface defects were negligible when compared with the catastrophic surface destruction that occurred when "as received" starch-oil coated SiO_2 fiber was heated.

Some similarly drawn but uncoated SiO_2 fibers were obtained from G. E. Lamp Glass Dept. (0.4 mil diam.) and from Libby Owens Ford (0.04 mil diam.).

TABLE I

EFFECT OF DESIZING AND SUBSTITUTION OF HIGH TEMPERATURE LUBRICANT
ON THE TENSILE STRENGTH OF 15C 4/3 SiO₂ YARN

Yarn Treatment	Room Temperature Tensile Breaking Load (Kgm)				Reference	
	r.t.	Dried 110 C	1 hr. 500 C	16 hr. 500 C		1 hr. 650 C
As received*	10.4	15.3	43.0	1.0		VI, 12a; IV, 23
(oil lubricated)				(3.8)		
Desized	8.6	12.3	6.3	6.7	1.6	VI, 12a; IV, 23, 25
(oil lubricated)	(9.3)			(7.7)		
Desized, Mg-methylate treated	8.8	16.9	10.2 8.5	10.5	8.3	VI, 12a IV, 25
Desized, Dri-Film treated	7.8		4.6		no	IV, 25
Desized, Zn-stearate treated			8.0 (at 500 C)			VII, 88

* In the "as received" condition the SiO₂ yarn fibers were coated with a starch-oil film which served as a lubricant and protected them from self abrasion damage.

The "as received" strength of the yarn varied from spool to spool and more widely from batch to batch.

The yarn batch used in most of the tests shown above was particularly weak "as received".

In electron micrographs these fibers appeared to have developed minute pores, after heat treatment at 500 C. But this effect, when further magnified, seemed to consist of a system of tiny ridges suggesting a very thin surface skin covering a slightly contracted interior volume. Certainly, the surface suffered no gross damage from heating. These observations strongly suggested that the starch-oil coating usually applied to the SiO_2 fiber was in some way causing the damaged surface, and consequent very low strength, of the heat treated SiO_2 yarn. (See Report IV, pp 28-35). Subsequently, we learned that the starch-oil finish contained an appreciable quantity of sodium, and that even a trace of sodium in contact with vitreous silica at elevated temperatures promotes divitrification and characteristic spalling of the glass surface.

SiO_2 YARN TREATMENT

A method, other than heat treatment, was devised for removing the offending starch-oil coating that was present on the SiO_2 yarn "as received". The method is fully described in Report IV pp 21-23. Essentially, it involves treating the yarn by repeated boiling in water to remove the starch, and vapor de-greasing with trichlorethylene. When carefully handled, the yarn appeared to suffer little real loss in low temperature strength as a result of removing the organic protective coating. (Report V pp 10-11). Cleaned yarn, after heating in the previously disastrous 500 C range, approached the strength of the yarn "as received" if the fibers were oil-lubricated before testing. However, it was noted that clean yarn tended to stiffen slightly and suffer from inter-fiber bonding when subjected to temperatures as high as 625 C.

Obviously some non-destructive fiber coating was needed to prevent sintering, and to provide lubrication for the fibers at both low and high temperatures. Desized yarn dipped in Dri Film (a mixture of chlorosilanes) retained some strength after being heated in the 500 C range but the treatment gave no

protection at higher temperatures. Pre-treating the cleaned yarn by dipping it in a 5% solution of magnesium methylate in methanol, followed by heating at 150 C to decompose the organic compound and produce a micro crystalline deposit of magnesium oxide, proved most effective in preserving the yarn strength when tested at high as well as at low temperatures. However, an excess of MgO deposited within the yarn bundle could be detrimental, causing some stiffening and even yarn damage in extreme cases. (See Reports IV pp 24-26; V pp 11-13; and VI pp 12-15)

Several other materials and methods were briefly tested as possible high temperature fiber protectors. (See Reports III pp 23-24; V pp 39; VII pp 80-88) These included impregnation of the yarn with copper compounds, cadmium iodide, or water soluble magnesium salts, treatment of the yarn with a low-strength magnesium-aluminum-phosphate binder, decomposition of CrO_3 to deposit Cr_2O_3 , and coating the yarn with aluminum or with metal stearates. Of these, the latter appears to offer the greatest promise if some means of coating individual fibers with a very thin stearate film can be devised. Such a coating would provide not only initial inter-fiber lubrication and subsequent high temperature deposition of a micro-crystalline oxide protective layer but also would serve initially as an inert barrier to moisture and possibly prevent the loss of yarn strength through chemical or physical interaction with the bonding cements used in the laminate structure.

EFFECT OF BONDING COMPOSITIONS ON SiO_2 YARN

In fabricating cement-bonded laminates, one of the first conditions encountered by the reinforcing fiber is immersion in the acidic or basic water-diluted cement slurry. As shown in Table II, a distinct but recoverable drop in the tensile strength of fused SiO_2 yarn is associated with the presence of moisture. What, then, is the effect of those acidic or basic solutions which

may be present in the bonding cement?

A few early tests confirmed our expectation that the SiO_2 yarn would be sadly weakened by exposure to alkaline solutions such as sodium silicate. Even yarn strands wet with alkaline-stabilized colloidal silica suspensions were notably weaker than when wet with distilled water. By comparison the wet strength of yarn treated with acidic solutions appeared to suffer only slightly. (See Report III p 12)

Particular interest was directed toward the effect of phosphoric acid since aluminum phosphate bonded cements, frequently containing unreacted H_3PO_4 , were principally used throughout the program. Tests showed that starch-oil coated yarn (as received), after being immersed in 30% H_3PO_4 at room temperature for 15 hours, washed, neutralized with a dilute ammonia solution, and dried at 70 C, required a tensile breaking load of 10.5 Kgm. This may be compared with the 13.5 Kgm required to break dried, untreated yarn taken from the same spool. A similar test, conducted with desized yarn, produced results showing the breaking load dropped from 22 Kgm to about 15 Kgm when desized yarn was acid treated. Such a difference in behavior between coated and uncoated yarn clearly demonstrated the protection afforded by the starch-oil coating but did not indicate whether it furnished protection from chemical corrosion or from physical abrasion. Fiber damage due to handling may well account for some if not all of the strength loss. (See Report VI pp 19-20) In another test "as received" yarn wet with distilled water broke under a 10 Kgm load while the strength of the yarn after 2 1/2 hours immersion in 60% H_3PO_4 appeared to be 9 Kgm. But the acid treated yarn, after being heated overnight at 90 C, could support only 7.5 Kgm as opposed to 18 Kgm for yarn similarly dried after water immersion. Following 1/2 hour exposure to either 200 C or 500 C the acid treated yarn broke when loaded with approximate-

TABLE II
EFFECT OF BONDING AGENTS ON THE TENSILE STRENGTH OF SiO₂ YARN (150 L/3)

Yarn Treatment	Heat Treatment		Load (Kgs.) to break yarn strand		Reference Report, page
	Test Temperature	Wet r.t.	dried 90°C 1/2 hr 200°C r.t.	1/2 hr 500°C r.t.	
As received, (14.0-16.0 Kgm)					
H ₂ O		11.0	26.0	21.0-23.0	VII 48, 75; III, 12
50% Sodium silicate soln.		5.0	18.0	21.0	VII 55
50% Colloidal silica soln.		7.0	brittle		III 12
60% H ₃ PO ₄		9.0	9.0	3.9	III 12
Al-phosphate soln. (100%)		9.0	7.5	21.0	III 12
bond 33 (unheated)		4.3	not dry	8.2	VII 48
bond 33 (pre-reacted)		9.5		21.5	VII 55
cement formulation 3		4.4	9.5	10.7	VII 55
bond A (self-heated)		9.7		30.0	III 12
bond A-3P		9.3	10.0(r.t.)	25.3	VII 52
bond MA3P		9.1	9.8(r.t.)	19.9	VII 75
bond-MA-3P		7.9	10.5(r.t.)	22.0	VII 75
Hydrolized ethyl silicate		9.5	29.0	29.0	VII 75
				1.0	III 12

COMPOSITION OF BONDING AGENTS CONTAINING ALUMINUM PHOSPHATE

	H ₂ O (cc)	H ₃ PO ₄ (cc)	Al(OH) ₃ (gm)	OTHER (gm)		Reference Report, page
				4.6 calcined Al(OH) ₃	4 Al ₂ O ₃ , 8 Zircon	
Bond 33(opaque after heating)	8	6				VII 54
Cement Formulation 3	4	6	4			III 13
Bond A (turbid)	4	6	4			VII 51
Bond A-3P(clear)		6	3			VII 71a
Bond MA3P		6	2.28		1.44 basic MgCO ₃	VII 72
Bond-MA-3P		6	3		0.9 basic MgCO ₃	VII 72
Al-phosphate solution (100%), a viscous solution obtained by dissolving 40 gm aluminum phosphate in 160 cc H ₃ PO ₄ (85%) heated at 250 C until boiling stopped.						III 12

ly 4 Kgm (Report III p 12). Thus it seems that even though orthophosphoric acid may not particularly harm the SiO_2 fibers at room temperature, its presence at slightly elevated temperatures can be disastrous.

If aluminum phosphate was present in the bonding solution, having been formed by reaction of aluminum hydroxide with phosphoric acid, or by solution of aluminum phosphate in the acid, a somewhat different result was obtained, even though the solution with which the SiO_2 yarn was treated was strongly acidic. As shown in Table II:

1. Yarn which was tested when wet with aluminum phosphate containing solutions had strength similar to yarn wet with phosphoric acid.
2. Treated strands that had dried at low temperature before testing were stronger, reflecting the effect of the highly polymerized, flexible, bond formed by aluminum phosphate solutions. Such a bond apparently helps to distribute the load and acts as an inter-fiber cushion.
3. If tested after having been heated for 1/2 hour at 200 C, eliminating mechanically held water from the flexible bond, many of the treated SiO_2 strands had strengths comparable to and in some cases exceeding the strength of thoroughly dried but untreated yarn.
4. A typical loss of strength due to crystallization of aluminum phosphate was shown by some of the treated strands when heated at 500 C.
5. Those yarn strands that retained good strength at 500 C had been treated with a magnesium - containing aluminum phosphate composition. The behavior of this group of samples is not totally explainable at present.

Aluminum phosphate-treated SiO_2 yarn strands heated for 1/2 hour at 500 C were usually quite brittle and suffered a consequent loss in strength. Microscopic examination revealed that the bonding phase had crystallized and lost flexibility. Individual SiO_2 fibers, rigidly held in this hard matrix, could no longer function independently. The bond, which at lower temperatures had served as a stress distributor, now acts as a stress concentrator. And yet there were two magnesium-aluminum-phosphate bond compositions in the series that caused very little harm at 500 C. The explanation for their exceptional behavior may involve:

1. less chemical reaction between bond and SiO_2 fiber due to the more effective neutralization of phosphoric acid by the magnesia incorporated

in the bond composition;

2. possibly more bond flexibility or plasticity at high temperatures than shown by aluminum phosphate alone;

3. development of blocky crystals in the bonding phase, giving less bond cohesion than produced by the needle shapes habitually formed by anhydrous aluminum phosphate;

4. the crystals may have thermal expansion characteristics compatible with the fused SiO_2 fiber. (See Report VII pp 48 - 55, 66 - 75)

In Table II you will note two bond compositions that produced unusually low strength when the treated yarn was tested while wet. These two (unheated 33, and cement formulation 3) were atypical in that they contained much unreacted, finely granular, material capable of abrading the SiO_2 fibers and thus destroying yarn strength. However, even yarn strands treated with these compositions followed the trend of the others by showing an improvement over wet strength when dried and exposed to 200 C. While phosphoric acid treated yarn obviously was degraded by this heat treatment (which failed to form a flexible bond between the fibers and succeeded only in accelerating chemical attack), the formation of the aluminum phosphate bonding compound was promoted by temperatures in the 200 C range. These bonding compositions in which the aluminum phosphate bond could form developed a firm though somewhat flexible adhesive phase which probably cushioned the individual SiO_2 fibers while holding them in place. In addition, the dried bond was capable of bearing some load. These physical attributes appear to compensate in some measure for any simultaneous chemical corrosion of the SiO_2 fibers which may have occurred due to the presence of reactive phosphoric acid.

The high strengths realized by yarn strands encased in the relatively weak bond formed at low temperature by hydrolized ethyl silicate shows that the readily friable silica gel deposited around the yarn fibers acted as a lubricant and stress distributor. After the 500 C heat treatment the high drying and firing shrinkage of this gel probably produced small, sharp edged particles strong enough to function as stress concentrators when the yarn

strand was tested. This, in addition to the probable surface spalling of starch-oil coated yarn when heated at 500 C could readily account for the very low yarn strength observed.

Summarizing this phase of the investigation it seems that, with but one exception, yarn samples treated with various types of adhesive-forming solutions or slurries and tested at 500 C (or at room temperature after exposure to 500 C) displayed a disastrous loss of strength. In most instances this appeared to be due to loss of fiber integrity. Whether this resulted from chemical interaction between the fibers and the bond or was due simply to a physical encapsulation of fibers in a brittle matrix was not determined. The obvious remedy, however, seemed to be in either the discovery of a flexible inorganic bond, stable at high temperatures, or the development of a treatment for the yarn that would prevent penetration of the binder into the interior of the fiber bundle and thus preserve a portion of the SiO₂ yarn strength.

PROTECTIVE YARN ENCAPSULATION

Considerable effort was devoted to testing various means for preventing the penetration of the bonding cement into the interior of the reinforcing fiber bundle. Such protection would prevent degradation of yarn strength due to interaction between individual fibers and the bond at high temperatures and also would preserve the yarn strength during fabrication of laminate structures, allowing the desired pre-stressing techniques to be used. To test the efficiency of films in protecting the yarn from harm during its fabrication into laminates, treated strands of the yarn were given a 180° bend before being dipped in the binder for 15 seconds in the bent position. The strength of the yarn was then tested in tension.

As a result of such tests it was found that low viscosity liquids such as silicone oils, mineral oils, etc., were not particularly effective. Solid,

non-extensible, coatings such as paraffin failed by cracking. Good yarn envelopment was obtained using somewhat elastic materials such as: Epolines (Eastman Chemical Prod.) hot melt, viscous, low molecular weight, polyethylene and polyethylene oxide compositions; Pliobond (Goodyear Tire and Rubber Co.) a solvent solution of phenolic-rubber which tends to "skinover" leaving lumps on the fiber; and Peele-Kote (Munray Prod.) a solvent solution of highly plasticized polyvinyl chloride which is easily applied as a thin, extremely flexible, encapsulating film. Yarn dipped in Dri-Film SC77 (G.E. Silicone Products Dept.) a mixture of chlorosilanes, was found to be excellently protected but so water repellent that it failed to pick up the bonding cement. (See Reports III pp 30-34; and IV pp 40-43)

For one reason or another none of the above protective treatments were sufficiently effective to allow proper pre-stressing of the reinforcing fibers during the fabrication of cement bonded laminate samples. However, a final test was made using heat-cleaned fused SiO_2 12 end roving heavily impregnated (20-25%) with silicone resin (Dow Corning DC-2106), as suggested in the WADC Report 58-298, May 1958. With this prepreg it was possible to form filament wound laminate samples using a Kidde compensator as a tensioning device exerting up to 5 pounds tension. Improved coating techniques may allow a reduction in the resin content which, at present, seems unnecessarily high. (See Report VIII pp 17-18)

Zinc stearate, which was previously mentioned as a possible low and high temperature lubricant, was also tested as a protective coating on SiO_2 yarn. A 26 Kgm tensile load was required to break a zinc stearate impregnated yarn strand coated with aluminum phosphate bonded cement. Unprotected yarn, when coated with cement, broke under a load of only 8 Kgm. (See Report VII p 88) This protective method has yet to be tested in laminate structures.

FIBER STATUS

Our survey of commercially available continuous filament reinforcing fibers for high temperature laminates has shown that "E" glass is unsuitable because of its relatively low softening temperature. The more refractory Refrasil (96% SiO_2) is structurally weak. Continuous fibers drawn from fused SiO_2 appear, at present, to provide the best available combination of low and high temperature strength. Maintenance of this strength requires that the fibers be protected at all times from abrasion and from degradative chemical attack. This can best be accomplished by individually coating the fibers with a thin, continuous, protective film as they are being drawn.

The identity of this perfect protective material is not yet known. Its discovery probably would require a separate development program. But we do know that the material must be alkali-free, must be applicable as a very thin continuous film, must be flexible, and provide low temperature lubrication. It cannot be water soluble nor strongly hydrophobic, and should not react readily with acidic solutions at low temperatures. Ideally, the material should not decompose at high temperature (if we could find this one our bonding problem would be answered, too), but if pyrolysis does occur, the resulting ash must be non-abrasive, highly refractory, and as nearly unreactive with the SiO_2 fiber as possible at high temperature.

Assuming that adequate protection for the fused SiO_2 fiber can be accomplished, so that its strength is maintained in the laminate structure, the problem of fully utilizing the strength of the fiber reinforcement remains. Unfortunately for our purpose, fused SiO_2 has much too low an elastic modulus. Its extension under load soon exceeds the extensibility of most inorganic bonding cements that might be used in the laminate structure. The laminate

fails under relatively small loads due to bond rupture. Theoretically, there are two solutions for this difficulty. First, use reinforcement fibers having a higher elastic modulus. Flexural strength tests on a number of experimental laminates demonstrated that, although monel wire reinforcement (having more than double the elastic modulus possessed by the commonly used "E" glass) substantially improved the strength of ceramic bonded laminate samples, the only high modulus ($16-18 \times 10^6$ psi) glass fibers that were available for testing failed to do so. (Report VII pp 32-35) This failure may be due to low fiber extensibility, to brittleness, scratch sensitivity, or increased susceptibility to chemical attack by the binder. Whatever the cause, if such behavior of non-metallic inorganic fibers inevitably accompanies the desired high elastic modulus, we must turn to the second solution for improvement in laminate strength. The second possible means for utilizing more of the strength of the fiber reinforcement in a laminate structure is to use a more extensible bond.

INORGANIC BONDING MATERIALS FOR HIGH TEMPERATURE LAMINATES

One intuitively suspects that little extensibility may be obtained from a normally polycrystalline inorganic cement-type bond. It was hoped that a temperature stable inorganic polymer having some of the qualities of organic resins might exist. Inquiry succeeded only in discovering that such inorganic polymers are in the highly experimental stage with production on a gram quantity basis at present and, therefore, inadequate for our immediate need.

Shelving this line of approach for the time being, we concentrated upon developing a useful low-temperature-setting inorganic cement-type bond. Admittedly, a laminate structure in which such a bond is used would be incapable of utilizing the full strength of the reinforcing fibers. Though the presence of fiber reinforcement notably improves the flexural strength of the composite, failure of the bond marks the failure of the laminate. In such a system an increase in flexural strength of even a brittle bonding media should definitely improve the strength of the laminate structure. This glaringly obvious supposition was tested using a prototype laminate system ("E" glass roving as the fiber reinforcement in chemically neutral gypsum cement matrices having various strengths). Results from these tests showed that, roughly, a 50% increase in laminate strength was realized when a 30% higher strength matrix was used, provided that the bonding slurries were similar in consistency, allowing equal penetration of the fiber roving and equal reinforcement to bond ratio in the laminate structures. Indeed, the technique employed in forming the laminate test specimens appeared to play a large role in determining their strength. (See Report V pp 35-38)

Since most of the inorganic bonds investigated during the course of this project could not be tested alone, but only in reinforced laminate specimens, direct comparison of one bond with another was clouded by the effects due to

physical variation in sample quality as well as variations in yarn strength and reaction with the bonding cement. Thus we may only state that one bonded laminate was stronger than another, leaving the relative strengths of the several bonds in the realm of speculation. Most of our test specimens were filament wound on a standard form and contained an equal number of yarn strands as reinforcement. The techniques employed are briefly described in a later section of this report.

PHOSPHATE BINDERS

From inception to conclusion this project has almost exclusively used aluminum phosphate cements as bonding matrices for fiber reinforced laminates. Although from time to time a number of other bonding media were considered and briefly tested, the results obtained were invariably less promising than those produced by the aluminum phosphate bond. Exploration of its behavior and a continual search for means to eliminate its detrimental features have proved both frustrating and rewarding. Much remains unexplained, much needs yet to be discovered. At present we can offer only speculative answers to the questions of how, and why, the aluminum phosphate bonded laminates behave as they do.

First, let us consider the cement slurry. It is primarily composed of two phases, the adhesive solution, and the more or less unreactive particulate filler. In the following discussion we shall consider the adhesive solution as being the source of the bonding phase, though its possible high temperature reaction with material present as cement filler may contribute appreciably to the total bond formed.

Literature on the subject states that aluminum phosphate $\text{Al}(\text{H}_2\text{PO}_4)_3$ forms the strongest of the phosphate adhesives. This compound is readily soluble in water, giving a strongly acid solution. Hydrolysis and consequent

precipitation reportedly occurs if the compound is present in solutions having a pH greater than about 2.8. The literature also states that this mono-aluminum phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) loses all mechanically held water when heated to 215 F (103 C), and half of the water of crystallization at 460 F (238 C). The resulting amorphous product recrystallizes at temperatures above 600 F (315 C) and becomes anhydrous $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ when heated to 930 F (500 C). The anhydrous phosphate is quite stable up to 1290 F (700 C) but above this temperature some volatilization of P_2O_5 occurs. At 900 C the rate of P_2O_5 loss becomes appreciable but the superficial appearance of the crystals remains unchanged.

The following observations were made during a series of experiments more fully described in Report VII, pp 51-52, 66-75:

1. Diluted phosphoric acid (H_3PO_4) reacted readily and exothermally with aluminum hydroxide ($\text{Al}(\text{OH})_3$) at room temperature. Very limited, if any, reaction occurred when this acid was blended with 900 mesh fused alumina (Al_2O_3) at room temperature but, extremely, fine grained, poorly crystallized alumina, obtained by calcining $\text{Al}(\text{OH})_3$ at 1550 F, appeared to be more reactive. Low temperature heating promoted the reaction between 900 mesh fused Al_2O_3 or calcined $\text{Al}(\text{OH})_3$ and H_3PO_4 .
2. Stoichiometric proportions of $\text{Al}(\text{OH})_3$ and diluted H_3PO_4 , to yield $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$, reacted exothermally when mixed but failed to produce a clear solution unless heated. After heating to clearness the viscous solution could be diluted extensively without causing the formation of a precipitate. The reacted mixture, if dried at 80 C formed a firm, clear film which tended to be slightly hygroscopic. Such behavior suggests the presence of unreacted H_3PO_4 .
3. With gentle heating the maximum $\text{Al}(\text{OH})_3$ addition that reacted completely with H_3PO_4 appeared to be a mixture having the mole composition $1.32 \text{ Al}_2\text{O}_3 : 3 \text{ P}_2\text{O}_5 + \text{H}_2\text{O}$. This syrupy strongly acid liquid could be diluted without forming a permanent precipitate. A film of the mixture, applied on a glass slide, dried at room temperature to a clear, hard, non-hygroscopic, crack-free coating which was slowly soluble in H_2O . Despite its acidity, the non-hygroscopic behavior of the dried composition indicated that no active H_3PO_4 remained.
4. When $\text{Al}(\text{OH})_3$ and H_3PO_4 were blended to give a molar composition of $1.4 \text{ Al}_2\text{O}_3 : 3 \text{ P}_2\text{O}_5$ no amount of heating succeeded in removing the slight remaining cloudiness. Addition of H_2O to reduce the viscosity produced a voluminous white precipitate which disappeared when the excess H_2O was evaporated. The mixture dried firm at room temperature but developed drying cracks.

5. Although we found it impossible to obtain a completely clear solution containing more than $1 \frac{1}{3}$ moles Al_2O_3 to 3 moles P_2O_5 , it was possible to add to this at least 1 mole of MgO (in the form of basic MgCO_3) without producing a permanent, insoluble, precipitate. The resultant mixture was a somewhat acid, very viscous, goo. When diluted with water, a voluminous white precipitate was formed which disappeared at room temperature as the excess water evaporated. A hard, clear, cracked coating was obtained when the mixture dried on glass at room temperature.

6. Completely clear bonding solutions having the molar compositions $1 \text{ MgO} : 1 \text{ Al}_2\text{O}_3 : 3 \text{ P}_2\text{O}_5$ or even $0.65 \text{ MgO} : 1.32 \text{ Al}_2\text{O}_3 : 3 \text{ P}_2\text{O}_5$ could be considerably diluted without causing precipitation. These dried at room temperature giving clear, hard, crack-free coatings on glass.

7. When the dried films obtained from these bonding solutions were gently heated, they softened slightly and bubbled when the chemically held water was released (approximately 240°C). If carefully heated in this temperature range, the course of devitrification could be observed as the coatings became more and more cloudy, finally turning quite opaque and pale gray in color. No further change was apparent even when the films were heated above 500°C . Following devitrification at approximately 350°C , these films were quite insoluble in water and, when moistened, gave no reaction on pH indicator paper.

8. Petrographic examination of the heated coatings revealed that initial devitrification of the aluminum phosphate compositions resulted in a maze of needle-shaped crystals. These interlocking fibers perhaps contribute to bonding strength. Compositions that contained magnesium in addition to the aluminum phosphate formed short prism shaped crystals.

Some time was spent in exploring the bonding possibilities of the

$\text{FeO}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system which behaves similarly to the $\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ system in that clear solutions may be prepared that dry at room temperature to firm, non-hygroscopic, glassy films. These lose water and become insoluble when devitrified by heating at 200°C . Reaction between Fe_3O_4 and diluted $\text{H}_{3-x}\text{PO}_{4-x/2}$ (obtained by preheating H_3PO_4 to opalescence, and assumed to be predominantly HPO_3) gave the above results whereas reaction between Fe_3O_4 or Fe_2O_3 with H_3PO_4 did not. The maximum Fe_3O_4 content that could be reacted with HPO_3 to produce a fairly stable solution gave a ratio of 1.32 Fe ions; 3 PO_3 ions, which is identical to the aluminum to phosphate ratio present in solutions containing the maximum $\text{Al}(\text{OH})_3$ soluble in H_3PO_4 . At room temperature 1.0 mole Fe_2C_3 appeared to remain unreacted in a solution containing approximately 1.0 mole Fe_3O_4 to 10 moles HPO_3 . When a thin film of such a mixture

was placed on a glass slide, dried at room temperature, then heated at 110 C, the Fe_2O_3 reacted completely giving a transparent, hard, crack-free film that devitrified when further heated at 200 C.

Fused SiO_2 yarn strands impregnated with such solutions remained fairly flexible after drying at 110 C. When the treated yarn was flexed following devitrification of the iron phosphate "glass" at higher temperature the coating broke but the yarn fibers remained intact. Heating above 320 C caused the development of an appreciable amount of inter-fiber bonding and resultant yarn embrittlement. Such bonding may well be due to chemical reaction between the fused SiO_2 fibers and the dehydrated iron phosphate compound, since the low strength of the devitrified material seems inadequate to produce a strong physical bond at this temperature. (See Report VII pp 56-65)

ALUMINUM PHOSPHATE BONDED CEMENTS

A large number of aluminum phosphate cement bonded laminate samples were made using cement Formulation 3 as the "standard" laminate bond. This cement, and variations shown in Table III, was heated only by the exothermic reaction that occurred when $\text{Al}(\text{OH})_3$ was mixed with diluted H_3PO_4 . As may be seen from the representative compositions, in addition to the $\text{Al}(\text{OH})_3$ that was present in excess of the amount capable of reacting with the acid to form the adhesive $\text{Al}(\text{H}_2\text{PO}_4)_3$ solution, the cements were principally filled with finely divided granular particles. These particulate materials (fused Al_2O_3 (38-900) and 325 mesh milled zircon) were chosen primarily for their thermal expansion characteristics and without regard to their high temperature reactivity with the aluminum phosphate adhesive phase. With so much ground to explore during this project, the area concerning the effect of various particulate fillers in the cement was relatively neglected. It is one field that should be thoroughly investigated in any future work.

Casual observation revealed that cement mixtures of this type softened when exposed to normally humid atmosphere, after apparently having been completely dried by heating at 150 C. This hygroscopic behavior strongly suggested the presence of unreacted concentrated phosphoric acid. How could this be when more than sufficient $\text{Al}(\text{OH})_3$ for reaction with the H_3PO_4 was provided?

As previously discussed, even stoichiometric mixtures of dilute H_3PO_4 and $\text{Al}(\text{OH})_3$ designed to produce the adhesive $\text{Al}(\text{H}_2\text{PO}_4)_3$ complex in solution failed to react completely at room temperature and required heating before a clear solution was obtained. This behavior may be logically explained if we assume that the dilute H_3PO_4 in contact with agglomerated particles of $\text{Al}(\text{OH})_3$ first forms a coating of hydrated $2\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$, which is virtually insoluble except in highly acid solutions. With sufficient acid available, the coating reacts to form $\text{Al}(\text{H}_2\text{PO}_4)_3$ but this, too, gives a protective gel-like hydrate that is insoluble in solutions having a pH greater than 2.8. Thus the interiors of the original $\text{Al}(\text{OH})_3$ particles are multiply protected from the poorly ionized H_3PO_4 that may remain in the surrounding liquid. If the ionization of diluted H_3PO_4 is increased by heating, eventually all $\text{Al}(\text{OH})_3$ present will form soluble $\text{Al}(\text{H}_2\text{PO}_4)_3$ as a more or less viscous solution, depending on its dilution.

Now let us consider the adhesive phase used in the cement mixtures. This contains a much higher $\text{Al}(\text{OH})_3$ to H_3PO_4 ratio than required for the formation of $\text{Al}(\text{H}_2\text{PO}_4)_3$. At room temperature we can expect only partial reaction with the available acid (as explained above) and, since less acid is present to promote solution of the protective hydrates formed around the $\text{Al}(\text{OH})_3$ particles, more $\text{Al}(\text{OH})_3$ is isolated from possible reaction with the

remaining H_3PO_4 . If at this stage the cement is dehydrated, the effectiveness of the acid is suppressed, not only because less ionization occurs in concentrated solutions, but also because the $\text{Al}(\text{H}_2\text{PO}_4)_3$ that has formed makes the dehydrated solution so viscous that it is virtually a solid. In such an environment the acid molecules can't get around much any more and must remain inactive until the temperature is increased sufficiently to allow their combination with such material as may be present in their immediate vicinity.

Granting the presence of unreacted H_3PO_4 in the dried cement mixtures; can the particulate fillers used in the cement react with this acid at low temperature and thus protect the SiO_2 reinforcing fibers from acid attack?

A simple experiment failed to reveal any noticeable bonding between the grains of the most frequently used cement fillers (900 mesh Al_2O_3 and 325 mesh zircon) when they were moistened with concentrated H_3PO_4 and heated for 2 hours at approximately 165 C. Of the few other materials tested with H_3PO_4 , hematite (Fe_2O_3) appeared to develop a permanent bond at the lowest temperature (approx. 110 C). Quartz (crystalline SiO_2) formed a rather weak but definite bond between the H_3PO_4 -treated grains when heated at 165 C; though the literature gives 260 C as the minimum temperature for reaction between SiO_2 and H_3PO_4 to form $\text{Si}(\text{PO}_3)_2$. If H_3PO_4 reacts with crystalline SiO_2 at 165 C, in all probability it can attack the less stable fused SiO_2 reinforcing fibers used in the laminates at even lower temperatures. Heating for 10 minutes at 235 C appreciably strengthened the intergranular bond between quartz grains and developed a very strong bond in the H_3PO_4 - Al_2O_3 mixture but no bonding could be detected in the treated zircon specimen. (See Report VII pp 56-58) From the above it would seem that in our choice of alumina and zircon as fillers for use with the unheated, strongly acidic, aluminum phosphate solution we have arbitrarily subjected the reinforcing

SiO₂ fibers to low temperature attack by phosphoric acid.

Furthermore, the bonding efficiency of these cements (such as Formulation 3 that contain excess Al(OH)₃) may be low. As shown above, by tying up some of the phosphate in an insoluble form, the unnecessarily high Al(OH)₃ content could prevent formation of the maximum quantity of the soluble adhesive Al(H₂PO₄)₃ (the compound said to be responsible for the strong bond developed by aluminum phosphate cements). Also, if totally unreacted Al(OH)₃ remains, its notoriously high firing shrinkage at temperatures above 300 C could contribute appreciably to cement shrinkage and be the source of increased cement porosity.

EFFECT OF HEAT ON STRENGTH OF FORMULATION 3 - BONDED LAMINATES

When one considers the many things theoretically wrong with cement compositions of the Formulation 3 type one is amazed by the relatively good laminate strengths obtained. As shown in Table III, SiO₂ yarn reinforced laminates bonded with Formulation 3 cement had room temperature flexural strengths in the 15,000 psi range (after having been cured at 300 C for 1/2 hour) and reached 18,000 psi if measured at 500 C. Their strength at 600 C was almost 16,000 psi, and at 700 C they retained over 13,000 psi.

At the present stage of the game only speculative interpretation of the data in Table III can be offered. This table lists the representative flexural strengths obtained when testing variously heated filament wound laminate specimens, all of them bonded with the aluminum phosphate cement (Formulation 3) discussed above.

First let us consider the vast difference in room temperature flexural strength (7,100 vs 19,500 psi) shown by fused SiO₂ and "E" glass reinforced laminates that were cured for 2 weeks in a 2 mm vacuum at 125 C. That this strength difference did not reflect real weakening of the SiO₂ fibers is in-

TABLE III

REPRESENTATIVE FLEXURAL STRENGTH (psi) OF FILAMENT¹ WOUND LAMINATES
BONDED WITH CEMENT FORMULATION 3²

THERMAL HISTORY ³ OF LAMINATE PRIOR TO TESTING	TEST TEMPERATURE (held for 1/2 hr. before loading)				Reference Report, page
	r.t.	500 C	600 C	700 C	
<u>SiO₂ YARN REINFORCEMENT</u>					
125 C 2 weeks in vacuum	7,130	16,400			IV 39a
300 C 1/2 hr.(in mold)	15,600 12,700				III 37
300 C 1/2 hr.	15,000 15,600	17,900 18,200	15,800	13,400	V 18a VI 23a; VII 26a
300 C 1 hr.	15,400	16,300			VI 18a; VI 23a
500 C 1/2 hr.(in mold)	14,000				III 37
500 C 1/2 hr.	4,600	14,700			VI 18a; VI 23a
500 C 1 hr.	4,600	12,400			VI 18a; VI 23a
500 C 6 hrs.		12,600			VII 26a
600 C 6 hrs.			8,500		VII 26a
700 C 6 hrs.				9,000	VII 26a
<u>"E" GLASS YARN REINFORCEMENT</u>					
125 C 2 weeks in vacuum	19,500	8,100			IV 41a
300 C 1/2 hr.	10,300	6,700	7,600	7,000	VIII 12a
500 C 6 hrs.		5,700			VIII 12a
600 C 6 hrs.			7,300		VIII 12a
700 C 6 hrs.				7,800	VIII 12a
(1) SiO ₂ yarn 150 4/3 with starch oil coating as received or "E" glass yarn 150 2/2 with silane finish as received.					
(2) Formulation 3 Cement: 60 cc H ₃ PO ₄ , 40 cc H ₂ O, 40 gm Al(OH) ₃ , 40 gm Al ₂ O ₃ , 80 gm zircon.					
(3) Except where noted, specimens were dried in air at 80 C 7 days and at 150 C 3 days then taken from the mold before further heating.					

licated by the respectable 16,400 psi strength of the SiO_2 reinforced samples when tested at 500 C. The observed low laminate strength at room temperature probably can be attributed to some reaction between the cement and the starch-oil coating on the SiO_2 fibers that prevented the cement from hardening normally at 125 C. Indirect substantiation of this view comes from the observation that a cement mixture, in which starch-oil coated SiO_2 fibers (milled to pass 325 mesh) had been substituted for the usual zircon content, failed to "set" properly even after curing at 150 C for 1 month. (See Report IV p 43) Judging by the good flexural strength of the "E" glass reinforced samples we may conclude that no harmful reaction occurred between the acidic cement and the silane finish present on the "E" glass fibers "as received".

As mentioned previously, complete drying of the adhesive phase can appreciably improve the tensile strength of the yarn reinforcement. SiO_2 yarn soaked in the unheated acidic bonding portion of the cement (4cc H_2O , 6 cc H_3PO_4 , 4 gm $\text{Al}(\text{OH})_3$) supported a 30,000 gm. tensile load if dried at 200 C before breaking at room temperature, but failed to support one third of this load if tested before drying. Untreated yarn, after drying at 200 C, broke when loaded in the 18,000-23,000 range. (See Report VII pp 51-52)

Referring again to the room temperature flexural strengths of laminates listed in Table III, the SiO_2 reinforced specimens cured at 300 C before testing usually had strengths somewhat above 15,000 psi. Although only one lower value (12,700 psi) is shown in the table, such low strength was not unique among the many samples tested. The real surprise is the 14,000 psi flexural strength at room temperature shown by samples that were cured at 500 C in the metal laminating mold. (A number of similarly high values for other mold-cured laminate samples are shown in the reference report). Such laminate strengths are unknown among specimens that were removed from the mold before

firing at 500 C. These show average room temperature flexural strengths of only 4,600 psi.

How can we account for the appreciable strength differences that were found in laminate samples presumed to have been similarly heated? Could these different results derive from variations in the cement bond?

Let us summarize what we have learned. A concentrated solution of highly polymerized $\text{Al}(\text{H}_2\text{PO}_4)_3$ stiffens to a firm, flexible, glassy material when dried. All mechanically held water is removed by heating a few degrees above 100 C. This "glass" softens slightly with increasing temperature until, at approximately 240 C, half of the chemically held water is released. Formulation of insoluble $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ then begins at a somewhat higher temperature. Although the literature gives 315 C as the minimum crystallization temperature, the insoluble nature of numerous cement samples heated for extended periods between 250 C and 300 C indicates that complete devitrification of the "glass" can and does occur within this lower temperature range. At approximately 500 C, when the remaining water of crystallization is said to be released, $\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5$ is formed. The anhydrous crystals are reported to retain their shape and continuity even though heated above 900 C, at which temperature the compound begins to lose P_2O_5 at an appreciable rate.

In one series of experiments microscope slides were coated with clear concentrated solutions approaching the $\text{Al}(\text{H}_2\text{PO}_4)_3$ composition. These were heated on a hot plate after having been dried at approximately 100 C. If very slowly heated these films could be dried and at least partially devitrified without appreciable bubbling. Petrographic examination showed such films to be interlaced with fiber-shaped crystals, giving an intrinsically strong, possibly flexible, structure. If, however the coated slides were placed on the hot-plate pre-heated above 240 C, the rapid release of water reduced the

viscosity of the coating and produced excessive bubbling. If the temperature was sufficiently high tiny bubbles were "frozen in" by the almost simultaneous crystallization that occurred. Such a material could have very little strength or flexibility. From this it is quite evident that the condition of the bond does not depend solely on the maximum temperature achieved but is greatly modified by the rate at which the temperature is reached.

If we consider the room temperature flexural strength of the laminate specimens in the light of their thermal history, and correlate this with the probable effect of these temperatures on the physical character of the adhesive aluminum phosphate phase in the cements, we find it quite understandable that wide variations in strength could be produced by minor differences in the heat treatment. For instance, there are temperature gradients throughout any oven. The actual temperature a particular laminate sample might reach during its curing cycle would depend on a number of things such as: how long the oven door was open during the loading operation (allowing cooling to occur); how much cool material was loaded; what was its oven location; how were the samples stacked; which specimens were closest to hot surfaces such as walls, shelves, etc.?

As we have mentioned, immediate heating at temperatures above 240 C could result in such rapid release of water vapor that a poor strength bond would result. Since the inert fillers present in the cement provide a somewhat porous structure which allows the vapor to escape readily, gross bubbling would not occur, but the formation of microscopic bubbles could readily reduce the strength of the cement. The rate at which the cement devitrified certainly would effect the crystal structure formed by the adhesive phase and, consequently, the bond strength. Though improbable, it is conceivable that the adhesive phase in some of the cement bonded laminates nominally heated at

300 C for 1/2 hour failed to devitrify completely and retained a portion of the strong glass-like material. Those laminates heated for 1/2 hour at 500 C while still in the metal mold, in all probability encountered a gradual temperature increase and possibly even failed to reach 500 C since the bulky mold would heat up relatively slowly. If indeed this was true, the adhesive phase in these cement bonded laminates could develop and retain a strong, well crystallized, semi-hydrated form. Free-fired samples, on the other hand when placed directly in the 500 C oven atmosphere were doubtless taken through the first stage of dehydration too fast and likely reached the 500 C oven temperature, where possibly disruptive dehydration occurs.

In the above discussion we have shown loss of strength by the cement bond to be one possible cause for the very low room temperature strength (4,600 psi) displayed by SiO_2 reinforced, aluminum phosphate cement bonded, laminates that initially had been too rapidly heated to 500 C. But this does not explain how these laminates can more than triple their strength if reheated to 500 C for testing. Obviously one or more temperature induced phenomena must be responsible for this happy result. There are three possible candidates:

1. The relatively high thermal expansion of the aluminum phosphate cement and the negligible thermal expansion of the fused SiO_2 fiber reinforcement produces a thermally induced tensile stress in the fiber reinforcement and an equal compressive stress on the cement matrix. Consequently, when the strength of the laminate is tested at temperature, the reinforcement bears the total applied breaking load until elastic extension of the fibers relieves the compressive stress that was imposed on the bonding matrix. Thereafter the load is shared until the strength limit of the matrix is reached and, assuming a brittle matrix, the cracks formed are propagated through the laminate and result in failure.
2. High temperature may lower the elastic modulus or allow greater extensibility in the cement bond making it less brittle. If this condition exists, the matrix would assume a smaller share of the load, allowing more of the stress to be placed on the high strength fiber reinforcement. In addition, with such a matrix serving as a bond between individual fibers, the stress distribution on the individual fibers could

more readily be equalized.

3. At elevated temperatures the SiO_2 fiber itself is undoubtedly less brittle. This serves to reduce its notch sensitivity so that the fiber degradation that may have occurred from acid attack, surface spalling, or abrasive damage, has less influence on fiber strength than at room temperature.

Although all three may contribute to the observed high temperature strength of the laminates, only the first can be extended readily to explain the limited reduction in high temperature strength that accompanied longer high temperature curing cycles. As shown in Table III, SiO_2 reinforced laminates cured at 500 C before testing at 500 C had decreased strength if heated for 1 hour instead of 1/2 hour (dropping from about 14,500 to 12,500 psi), but no further loss occurred even though the laminates were aged for 6 hours at 500 C. With aging and testing temperature increased to 600 C the high temperature flexural strength of laminates aged for 6 hours decreased to 8,500 psi, but no further loss was encountered if the temperature of test and cure was increased to 700 C. In fact, a slight, but possibly real, increase in strength was obtained at this higher temperature.

At first glance we might suppose that increasing time at aging temperature provided a greater opportunity for the phosphate binder to attack and weaken the SiO_2 reinforcing fibers. But if this were so we should observe a marked strength decrease in those laminates that had been cured for 6 hours at 500 C as compared with specimens cured at that temperature for 1 hour only. Since this was not found to occur, some other mechanism must be responsible for the observed behavior. There are two possibilities:

1. At any given temperature the SiO_2 fibers are capable of elastically supporting a given tensile stress but beyond this point a permanent, slow, deformation occurs which relieves the excess stress. As in the annealing of any glass, the rate of yield depends on the degree of stressing and on the viscosity of the glass. Both of these, in the laminate structure, are functions of the temperature.
2. For any given temperature and time, the cement bond undergoes a certain firing shrinkage because of chemical and physical reactions.

These proceed slowly toward equilibrium at a minimum temperature and are accelerated by higher temperatures.

Both of these mechanisms serve to relieve compressive stress on the cement and thus tend to weaken the laminate, but only by a certain amount, the limit for any given temperature being established by the equilibrium involved.

Further light may be shed on the strength determining mechanisms involved in the laminate structures by comparing the behavior of Formulation 3 bonded "E" glass reinforced laminates with results obtained from SiO_2 yarn reinforced samples in which the same cement bond was used. Because "E" glass has a much higher thermal expansion than possessed by fused SiO_2 we may expect that at high temperature the compressive stress imposed on the cement bond in an "E" glass reinforced laminate would be less than when SiO_2 yarn is used. For this reason we would expect "E" glass laminates to have less strength at high temperature than SiO_2 reinforced samples. The effect was shown by laminates cured for 1/2 hour at 300 C before measuring at 500 C ("E" glass, 7,600 psi vs. fused SiO_2 , 15,800 psi). But this dramatic difference virtually disappeared if strengths at 600 C, after 6 hours cure at temperature, are compared ("E" glass 7,300 psi vs. fused SiO_2 8,700 psi). The change cannot be attributed to the behavior of the cement bond since this was the same in both laminates, nor can we suppose it due to the state of the reinforcing fibers at test temperature since in all cases this was the same. The most logical explanation appears to be that, during the 6 hour curing period at 600 C prior to testing at 600 C, the SiO_2 fiber reinforcement in the laminate sample was annealed, thus relieving the compressive stress its low thermal expansion had imposed on the bonding cement. The fused SiO_2 in the laminates that were only exposed to 600 C for the 1/2 hour period before testing was not completely annealed in this time but the "E" glass, with its lower anneal-

ing temperature, apparently achieved a stress-free state during this heat treatment. In fact, the low strengths obtained when testing "E" glass laminates at 500 C indicate that short term exposure to this temperature is sufficient to almost completely anneal the glass.

Examination of the "E" glass reinforced samples that were broken at 700 C showed that the laminates actually failed by plastic flow (See Report VIII pp 12-15). Since this was the case, the glass could not have contributed much to the total strength of the laminate and we have a qualitative picture of the flexural strength of the cement itself at 700 C. It may be stretching a point, but the increase in strength of the "E" glass reinforced laminates aged at increasingly high temperature (500, 600, and 700 C) for 6 hours suggests that the strength of the cement bond was improved. The same conclusion may be drawn from the slight increase in laminate strength shown by the SiO_2 reinforced laminates that had been cured at 600 and 700 C for 6 hours before testing at elevated temperature. Unfortunately we have no data on such laminates at room temperature and so do not know whether the apparent increase in strength was due to temperature induced bond extensibility or to better sintering between the bonding particles.

If this analysis of laminate behavior at elevated temperatures is correct, we are faced with a definite time-temperature limitation insofar as maintaining good laminate strength at high temperature is concerned. Improvement could be achieved by:

1. Employing a new reinforcing fiber having a much higher annealing temperature than fused SiO_2 .
2. Alteration of the bonding cement to provide greater extensibility and/or increased tensile strength.
3. Preserving the initial strength of the reinforcement by preventing possible acid attack on the reinforcing fibers.

TABLE IV

REPRESENTATIVE CEMENT COMPOSITIONS USED IN LAMINATE FABRICATION
(SiO_2 Yarn 150 4/3 "as received" used as continuous filament reinforcement)

and
FLEXURAL STRENGTH OF THE RESULTING LAMINATES

CEMENT FORMULATION NO.	(Bonding phase unheated)			(Bonding phase pre-reacted)		
	1.	2.	3.	33-V3	A-3P	MA-3P 1/2MA-3P
BONDING PHASE						
Phosphoric acid (85%) (cc)	60	60	60	60	60	60
Water (cc)	40	40	40	80	90	90
Aluminum hydroxide (gm)	40	40	40	46	30	30
Calcined $\text{Al}(\text{OH})_3$ (gm)						
Basic MgCO_3 (gm)						7
FILLER MATERIALS						
Aluminum oxide (900 mesh) (gm)						
Zircon (325 mesh) (gm)	80	60	40	24.2	135	30
Aluminum phosphate (gm)		20	80	270	270	270
Silica microfiber (gm)						15
LAMINATE FLEXURAL STRENGTH (psi)						
at room temp. after 30 min.	3,600	14,200	12,100	8,600	9,300	5,800
at 300 C						
at room temp. after 30 min.	2,400	3,800	6,200	7,800	6,700	5,700
at 500 C						
at 500 C after 30 min.	6,600		17,900		11,200	9,700
at 500 C						
REFERENCE (Report, page)	VIII, 20a	II, 9, 13	II, 9, 13	VII, 55	VIII, 52a 53a	VIII, 52a 53a

TABLE IV (cont.)

BONDING PHASE	CEMENT FORMULATION NO.	(Bonding phase unheated)							
		3-3M	3-3A3M	3-3A	3-6A	3-3S	Z-3A	Z-6A	Z
Phosphoric acid (85%) (cc)		60	60	60	60	60	60	60	60
Water (cc)		40	40	40	40	40	40	40	40
Aluminum hydroxide (gm)		40	40	40	40	40	40	40	40
FILLER MATERIAL									
Aluminum oxide (900 mesh) (gm)		40	40	40		40			
Zircon (325 mesh) (gm)		80	80	80	80	80			
Mica (1000 mesh) (gm)		9	9						
Asbestos floats (gm)			9	9	16		5	11	
Silica micro fiber (gm)						9			

LAMINATE FLEXURAL STRENGTH (psi)

at room temp. after 30 min.	10,700	12,700	19,900	19,100	17,500	7,600	7,800	3,600
at 300 C								
at room temp. after 30 min.						7,000	10,000	2,400
at 500 C								
at 500 C after 30 min.	10,400	15,300	13,700	24,000	18,400	15,400	11,700	6,600
at 500 C								
at 500 C after 6 hours						12,000	13,000	4,700
at 500 C								

REFERENCE (Report, page)

VII,25 VII,25 VII,19 VII,19 VI,26a VIII,20a VIII,20a VIII,20a

MODIFICATION OF CEMENT FORMULATION 3

Toward the conclusion of the program several cement compositions were prepared using laminar particles (mica or glass flake) as part or all of the cement filler. This was done with the intention of introducing minute planes of weakness in the cement to give it an artificial "extensibility". By this means it was hoped that the reinforcing fibers in a laminate structure bonded with such a cement could be induced to accept more of the flexural load and thus produce stronger laminates. (See Reports VII pp 24-26, VIII pp 23-24)

As shown by selected compositions (3-3M, 3-3A3M) in Table IV the results of flexural strength tests on these flake-filled laminates indicated that (at least with the bond used) intentional weakening of the cement by micro-cracking also weakened the laminate. By including asbestos micro-fibers in the cement filler, to act as barriers to crack propagation, some of the lost strength was recovered. In the present state of the art, this approach appears to be fruitless, but when other bonds for the cement have been developed perhaps a reappraisal of controlled microcracking may yield beneficial results.

In an effort to mechanically strengthen the cement by inclusion of short fiber-shaped particles as a portion of the cement filler, a number of materials were tested in addition to the fairly successful asbestos and silica micro-fibers shown in Table IV. Fiber Frax (Carborundum Co.) potassium titanate (DuPont) and wollastonite F-1 (Cabot Corp.) were tried as well as some longer fibered asbestos minerals including paligorskite, an asbestos-like mineral stable at 650 C. Long fibers could not be properly dispersed in the cement slurry. They require considerable reduction in size to put them into useable form, a process hardly worth the trouble except in the case of paligorskite. This mineral is certainly worth further investigation since it may provide the high temperature strength that asbestos is naturally

incapable of due to deterioration of the crystal structure at temperatures above 450 C. (See Reports V pp 24-26, and VI pp 27-28)

ASBESTOS IN ALUMINUM PHOSPHATE CEMENTS

Considerable advantage in strength was gained by small additions (3% by weight) of micro fibers to the original cement composition. Larger additions were prohibited due to a rapid viscosity increase that made the cement totally unworkable. Several new formulations were tried in which the particulate fillers were reduced, or totally eliminated, and replaced with short fibered asbestos. Although relatively poor strength accompanied the use of asbestos as the only cement filler, the best laminate strengths so far realized were obtained when the SiO_2 fiber reinforcement was bonded with a cement formulation (3-6A) containing 6% by wt. asbestos floats, and using zircon as the particulate filler. With this composition we have apparently achieved a reasonably strong laminate structure (24,000 psi flexural strength) that may be used, at least for short periods of time, at temperatures up to 500 C. (See Reports VI pp 27-28, and VIII pp 20-23)

At present we cannot certainly say by what mechanism the asbestos fiber aids in producing higher laminate strengths. Quite possibly its contribution is in part mechanical, with the micro-fibers serving as barriers to retard crack propagation. Also, these flexible fiber shapes would cause less abrasive action than granular cement fillers and thus be less harmful to the strength of the SiO_2 fiber reinforcement. Another plus feature could derive from the effect asbestos may have on the firing shrinkage and/or the thermal expansion of the cement bond. In addition, we know that asbestos (a hydrated magnesium aluminum silicate mineral) reacts to some extent with phosphoric acid. Exactly what effect this may have on the properties of the soluble adhesive phase is still open to question but, as discussed in the section

devoted to the aluminum phosphate bond (pg. 11) we have observed that SiO_2 fibers maintain their strength at 500 C when treated with a pre-reacted magnesium-aluminum-phosphate bonding composition, whereas they are appallingly degraded by aluminum phosphate alone. (See Report VII pp 66-67, 71-75) Beyond any doubt, if further advances are to be made in ceramic bonded laminate technology, the puzzle presented by the effect of asbestos on laminate strength must be solved. The answer could lead to a true understanding of the fundamentals involved in laminate behavior.

LAMINATES BONDED WITH PRE-REACTED PHOSPHATE ADHESIVES

By using pre-reacted aluminum phosphate solutions in the bonding cements, a somewhat different approach was made to the problem of improving both high and low temperature laminate strength. In such solutions no H_3PO_4 remained free to attack the reinforcing fibers in the laminate structure and no unused $\text{Al}(\text{OH})_3$ or insoluble aluminum phosphates were present to act as undesirable filler additions in the cement. (See Reports VII pp 66-79, VIII pp 53-55) The preparation of such adhesive solutions (A-3P, MA3P, and MA-3P) and their effect on the tensile strength of fused SiO_2 yarn at elevated temperatures is discussed on Pg. 11 and shown in Table II. The pre-reacted adhesive composition 33 also discussed contained undissolved particles because an excessive quantity of Al_2O_3 was used. These, or similar, adhesive solutions were blended with inert particulate fillers to form the cement bonds in SiO_2 yarn reinforced laminate samples whose flexural strengths after heating were determined. The cement compositions and laminate strengths obtained are shown in Table IV where they may be compared with the extensively used cement Formulation 3.

Such comparison immediately shows that laminates employing the pre-reacted bond compositions are not as strong as the laminates bonded with the Formulation 3 cement if they are measured at 500 C, or at room temperature after being

heated at 300 C. But their room temperature flexural strength following heating at 500 C is higher than that shown by the Formulation 3 bonded laminates. Their percentage loss in room temperature flexural strength, as a result of having been heated at 500 C instead of at 300 C before testing, is comparatively small. This is, indeed, a giant stride in the right direction.

The lower strengths obtained when these cements (33-Y3, A-3P, MA-3P, and 1/2 MA-3P) are used in laminates may not honestly represent the strength of the pre-reacted adhesive phase as compared with the adhesive formed in the Formulation 3 cement. The ratio of adhesive to filler in the pre-reacted compositions differs greatly from that employed in the much used Formulation 3 cement. We hope that a vast improvement in cement strength may be realized when the optimum adhesive to filler ratio is discovered. Particular trust is placed in the development of cement bonds employing a pre-reacted adhesive phase of the magnesium-aluminum phosphate type. Among all of those tested, these alone allowed the fused SiO_2 yarn to maintain its tensile strength when tested at 500 C. (See Table II) We have not yet discovered why this is so.

COLLOIDAL BINDERS, EXTENSIBLE BINDERS, LOW TEMPERATURE GLASS BINDER

Several tests were made using colloidal SiO_2 , in liquid suspension, as bonding cement for fiber reinforced laminates. Carborundum Corp. binders (TW, and QD 180) developed for use with Fiberfrax yarn were among those tested. None of the samples displayed much strength (1800-5600 psi) possibly because of low bond volume, rather than any detrimental effect the somewhat alkaline colloid suspension may have had on the SiO_2 fibers.

An attempt was made to form a magnesium silicate bond in situ by first treating the SiO_2 yarn with a 5% magnesium methyllate-alcohol solution then dipping the yarn in colloidal silica suspension. This produced a bulky gel containing little solid material. After winding, drying, and firing the

laminates at 600 C, alternate dipping in the two solutions and refiring was tried in an effort to fill the void spaces with more bond material. The average 3400 psi flexural strength obtained was not encouraging (See Report VII pp 36-39).

Since bond extensibility is a highly desirable quality in cement used with fiber reinforced laminates, a number of combinations were tried in the hope that a stretchable, temperature stable, semi-inorganic composition could be developed. The possibility of producing some such temperature resistant material was indicated by the continued water repellency shown by Dri Film treated SiO_2 yarn, after it was heated at 500 C. Combinations of chlorosilanes (Dri Film SC77) with SiO_2 , $\text{Al}(\text{OH})_3$, or the graphite-like Zirklor (ZrCl) obtained from the Chicago Development Corp., yielded no promising materials. (See Report V pp 30-34)

Some interesting results were obtained from attempts to form a non-hydrated aluminum phosphate cement by mixing $\text{Al}(\text{OH})_3$ with P_2O_5 in a silicone fluid vehicle. Of the several silicone fluids tried, only SF-96 (G.E. Silicone Products Dept.) did not gel immediately when brought in contact with dry P_2O_5 . In fact the SF-96 mixture failed to harden during low temperature curing and remained hygroscopic after firing for 1/2 hour at 500 C. Even so, an average flexural strength of 6400 psi was observed when specimens were broken at 500 C. (See Report VIII pp 50-52)

Since glass of any sort has greater extensibility than poly-crystalline material appears capable of showing, a glass-bonded reinforced laminate should produce a strong structure if: (a) the bonding glass has a lower elastic modulus and an extensibility at least equal to that possessed by the vitreous reinforcing fibers; and (b) the bonding glass does not react with or dissolve the reinforcement. A test of such a system was made using one of the low

melting (arsenic-sulfur-tellurium) glass compositions developed by Bell Laboratories and available from American Smelting and Refining Co. This glass, when heated in a N_2 atmosphere at 350 C, had a sufficiently low viscosity to allow strips of Silica 181 Cloth to be imperfectly impregnated by dipping in the molten glass bath. Laminate samples were formed using 7 cloth layers stacked in a press heated to 365 C. Contact pressure, applied for 5-10 minutes at temperature, caused excessive flow and produced bond-starved laminates. Despite their poor quality these samples, when tested at room temperature, had an average flexural strength of 10,700 psi (which compares very favorably with the 4,900 psi obtained from SiO_2 cloth reinforced laminates bonded with the aluminum phosphate cement Formulation 3). (See Report VIII pp 44-46)

The beneficial effect of using a non-crystalline (inorganic glass) bond appears to be unobtainable for fiber reinforced laminate structures that must retain their strength at 500 C or higher. The bonding glass must have sufficient rigidity to hold the reinforcing fibers in place at the use temperature. Here we are caught in a fine dilemma: to provide the low viscosity initially required for good bond formation, the laminate fabrication temperature must be much higher than its intended use temperature; but such temperatures somewhat soften the reinforcing fibers, and promote solution of the fiber in the bonding matrix. Assuming these difficulties could be avoided, the high fabrication temperature required far exceeds the reinforced plastic fabrication temperature range which was set as one of the goals for this project.

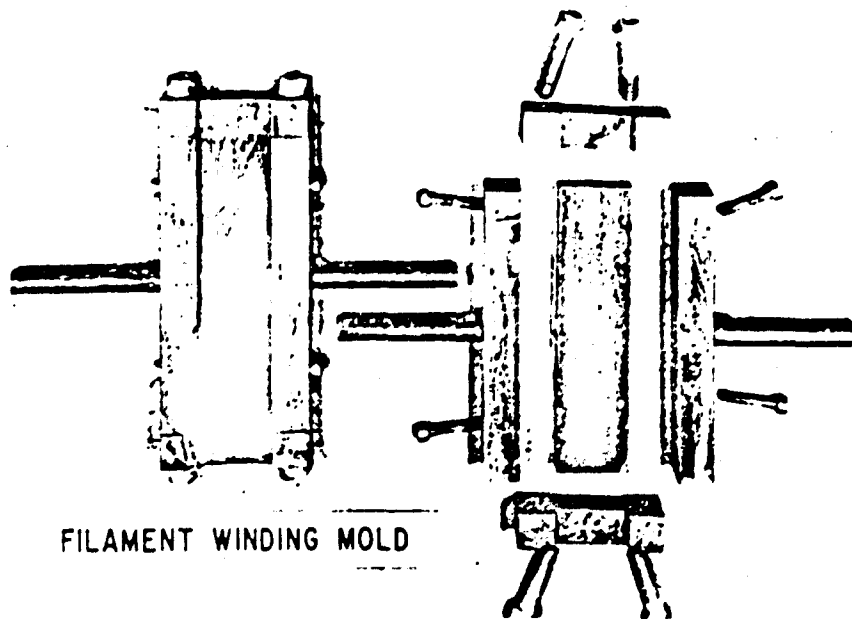
Laminate Fabrication by Hot Pressing

Ignoring the fabrication temperature limitation, we made several attempts to form glass bonded laminate samples by the hot pressing technique to see what the results would be. We found that, if used singly in the absence of a bonding phase, neither an applied pressure of 500 psi nor a temperature of

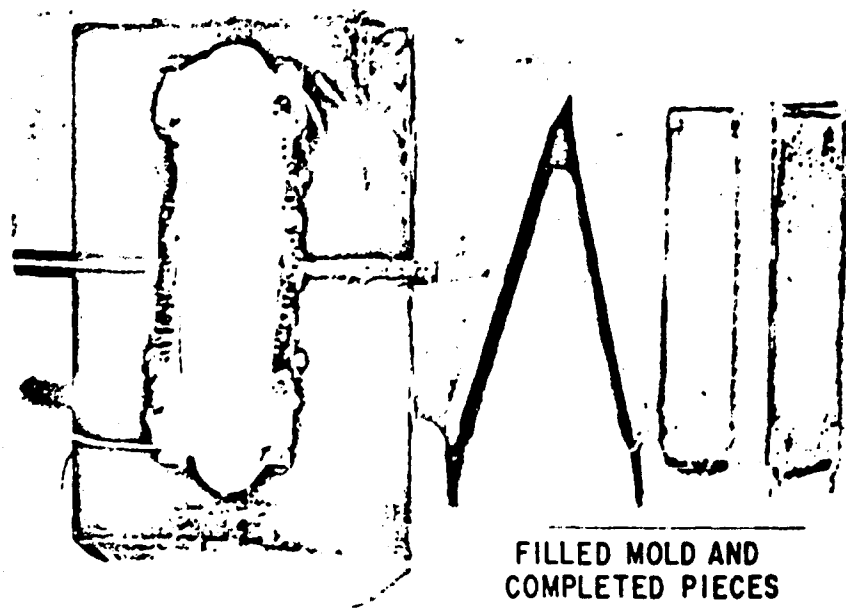
925 C unduly harmed the flexibility of desized fused SiO_2 yarn. However, yarn strands simultaneously subjected to this pressure and temperature formed a coherent mass that was extremely brittle due to inter-filament sintering. Threshold conditions for the occurrence of such degradation must be established if hot pressing techniques are to be used.

A lead borate glass frit (softening temperature approximately 450 C) was tried as a bonding matrix for SiO_2 yarn. Samples were formed by placing alternate layers of glass frit and SiO_2 yarn strands in a boron nitride coated metal die. After heating the filled die to temperature in a pot furnace, it was removed to an insulated chamber and loaded with a dead weight of from 6 to 15 psi. In order to obtain adequate sintering of the lead borate glass, temperatures of 550 C or above were required. If the temperature much exceeded 600 C, the strong bond developed between fiber and glass matrix appeared to destroy fiber integrity and resulted in samples that fractured in a brittle manner. Only those samples formed in the 550-600 C range broke without severing the reinforcing fibers completely. Although these samples contained a relatively low volume of fiber reinforcement, the room temperature flexural strength of the one sample tested was 3100 psi.

These results lead us to believe that hot forming at low pressure, though tricky, is a possible means for fabricating reinforced laminate structures bonded with other (higher temperature) glasses. (See Report II pp 14-17) One interesting possibility lies in the development of a low melting glassy frit that partially devitrifies, when properly reheated, to yield a more refractory glass bonded crystalline matrix (similar in behavior to the Corning Glass Co. Pyrocera cements).



FILAMENT WINDING MOLD



FILLED MOLD AND
COMPLETED PIECES

Figure 2
FILAMENT WINDING MOLD
-38a-

TECHNIQUES USED IN FABRICATING CEMENT BONDED LAMINATE SAMPLES

CEMENT PREPARATION

Most of the cement compositions used in the fabrication of laminates were prepared by mixing the dry ingredients with dilute H_3PO_4 at room temperature to produce a slurry having a creamy consistency. When small batches were desired they were mixed by hand with a mortar and pestle. It was more convenient to blend larger batches in a ball mill, using a 15-20 minute milling cycle, or simply in a container of suitable size using a drill press-driven propeller to do the mixing.

Those compositions in which a pre-reacted adhesive phase was used were prepared by first blending the $Al(OH)_3$ content with water to form a slurry. This was added slowly, with constant stirring, to the diluted H_3PO_4 contained in a Pyrex beaker of suitable size. The mixture was then clarified by heating. If the formulation called for magnesium carbonate it was gradually added, dry, to the reacted aluminum phosphate solution. Usually no further heating was needed to provide a completely clear liquid. The cement fillers were then bended with the solution to provide a slurry and, if required, water was added to give the mixture a workable consistency. (See Report VII pp 76-79)

FILAMENT WOUND SAMPLES

Accurately dimensioned filament wound laminate samples for flexural testing were obtained without machining by using a laminating mandrel. This consisted of a double-faced metal mold supplying two cavities (1" X 4" X 1/8") which permitted two samples to be formed under identical conditions. Those faces of the mold that would come in contact with the laminate were given a fluorocarbon, vinyl, or cellophane, coating to prevent sticking. Expanded

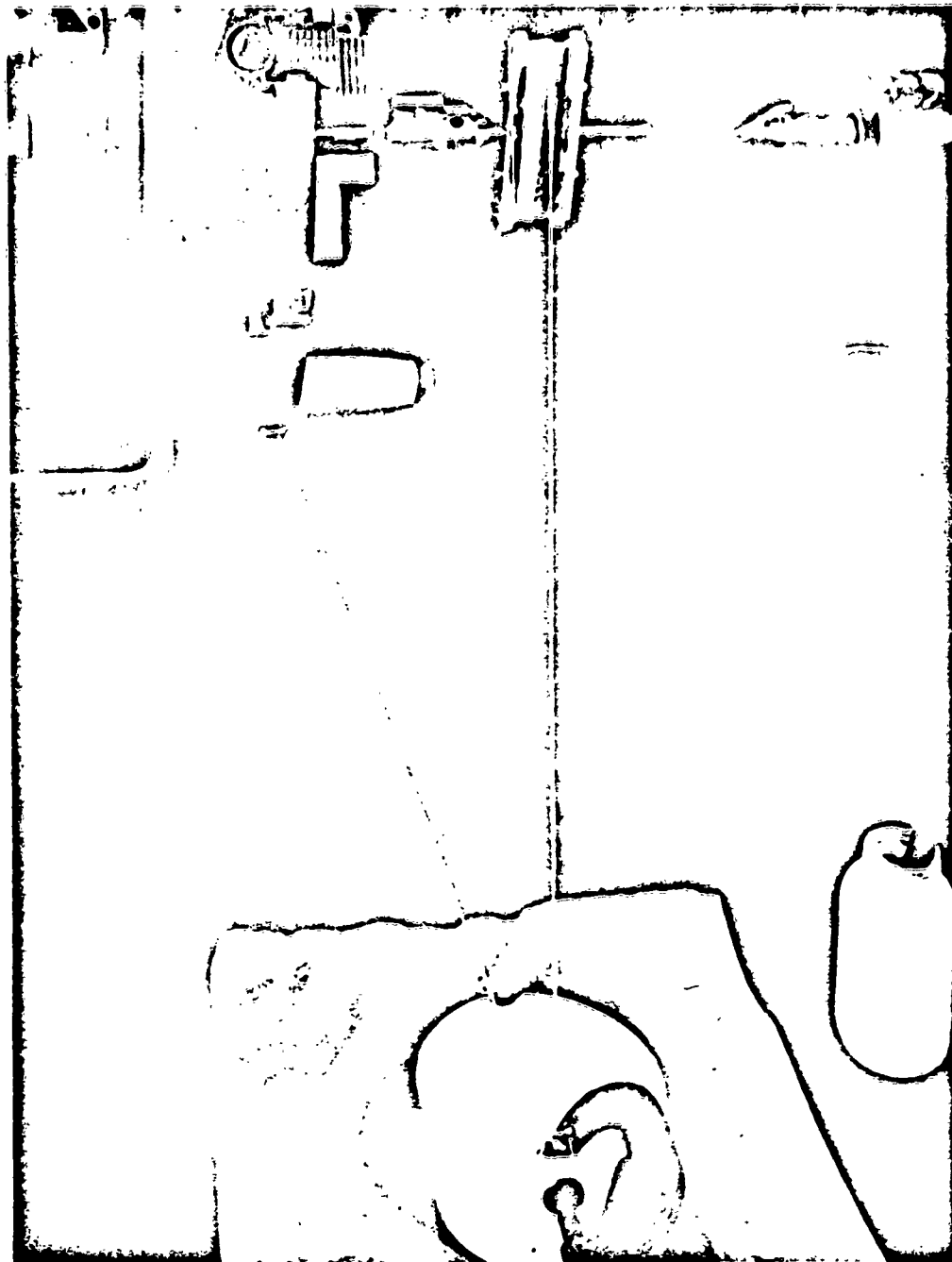


Figure 3
FILAMENT WINDING PROCEDURE
-39a-

and assembled views of the mold are shown in Fig. 2. The mold was rotated slowly on a lathe as the reinforcing yarn or roving (which had been drawn through a bath of cement slurry) was wound in place as shown in Fig. 3.

Usually samples were wound with only enough tension on the yarn to make the strands lie straight but some samples were made using a Kidde Compensator as a pre-tensioning device (See Report III pp 34-36). Unless the yarn was given a special protective coating to prevent strength degradation due to contact with the cement slurry, no more than 0.2 to 0.4 Kgm tension could be used without causing repeated yarn breakage; though the yarn, when tested dry, supported tensile loads of from 15 to 18 Kgm. Yarn provided with a good protective coating could be pretensioned with from 0.9 to 2.3 Kgm as it was wound on the standard sample mold.

The relatively large diameter and tight twist of the SiO_2 yarn (150 4/3) that was most frequently used as laminate reinforcement, prevented even stressing of the individual filaments and gave a corduroy appearance to the surfaces of the laminate samples. Smoother sample surfaces, better reinforcing structure, and more thorough impregnation of the 2400 filament strands should be obtained by using slightly twisted 12 end roving. But because the looser structure of this roving allowed more cement pick-up than encountered with the 150 4/3 SiO_2 yarn, it was more difficult to pack an equal number of reinforcing fibers into the mold. The mold was filled to capacity by 137 strands of the cement impregnated yarn. When roving was used only 100 strands filled the mold, if ordinary winding techniques were employed. If the excess cement carried by the roving was removed by continual wiping of the sample surface, and particular care was exercised in order to obtain even packing of the fibers in the mold, it was possible to make samples containing 137 strands of roving. Samples made in this way had a fiber content equal to that in the

yarn reinforced laminates. We were disappointed to find that the roving reinforced laminates, though beautifully smooth in appearance, were not superior in strength to those reinforced with yarn. This may be due to the increased amount of handling required, and consequent weakening of the fibers by the abrasive action of the cement.

Several samples were reinforced with silicone resin (DC-2106) impregnated fused SiO_2 roving which could be pre-tensioned to 2.3 Kgm without breaking. These specimens proved to have excellent room temperature strength (29,000 psi after curing at 300 C) and good strength when measured at 500 C (24,000 psi). (See Report VIII pp 17-19)

After the mold was filled (in most cases with 137 strands of cement impregnated SiO_2 yarn (150 4/3, 2400 filament), flat metal plates were placed against the exposed sample faces and clamped down in order to squeeze out excess cement and form flat exterior faces on the laminate samples. The assembly was allowed to dry at room temperature for one day before being placed in an oven at 80 C for one week. During this period, unless the atmosphere was extremely humid, the cement bond had hardened sufficiently to allow the exposed specimen ends to be cut apart and the two resulting samples removed from the mold. However, in order to eliminate any chance of sample warpage during subsequent heat treatment, we found it better to simply remove the face plates after completion of the drying period and further cure the samples for 72 hours at 150 C before separating them and removing them from the metal mold. Curing of the free samples may then be completed by 1/2 hour exposure at 300 C.

Although some experiments were made using a vacuum oven in an effort to shorten the drying time and/or lower the curing temperatures, the results were not particularly promising. (See Reports III pp 37-39; IV pp 40-43)

Sample preparation time was considerably shortened by drying the complete mold assembly for 4 days at 80 C, removing the face plates, and exposing the laminate samples to 300 C while still in the metal mold, but this technique caused deterioration of the organic lubricants used as mold release agents and thus subjected the laminates to possible damage. (See Report V p 18) In all probability an abbreviated 4 day drying cycle of the complete assembly at 90 C followed by overnight drying at 150 C, with face plates removed, would be sufficient preparation for removal of the samples from the mold for free firing at 300 C.

WET LAY UP FABRICATION

A few samples reinforced with fused SiO_2 181 cloth that had been heat cleaned at 400 C were fabricated by the wet lay up technique using eight cement coated cloth layers to give the required specimen thickness. The assembly was sandwiched between two lubricated flat metal plates to produce smooth surfaces and were cured in the usual manner. Flexural strength samples were cut from this layer cake and ground to size. Although the resulting surfaces were smooth and appeared quite free of voids, the apparent density of these laminates (1.4) was appreciably lower than the 1.8 normally obtained with filament wound samples.

The flexural strength of the cloth reinforced laminates was much lower than that of filament wound SiO_2 yarn reinforced samples. There are a number of reasons why this should be so: fiber damage incurred from heat cleaning and subsequent handling of the cloth; lower laminate density, indicating a greater number of voids; lower fiber content in the stressed direction; and the crushing effect of crossed fibers in the woven reinforcement. Of these, the first can be rectified by use of a proper protective film on the fibers, the second by using bag molding to improve the laminate density. (See Report

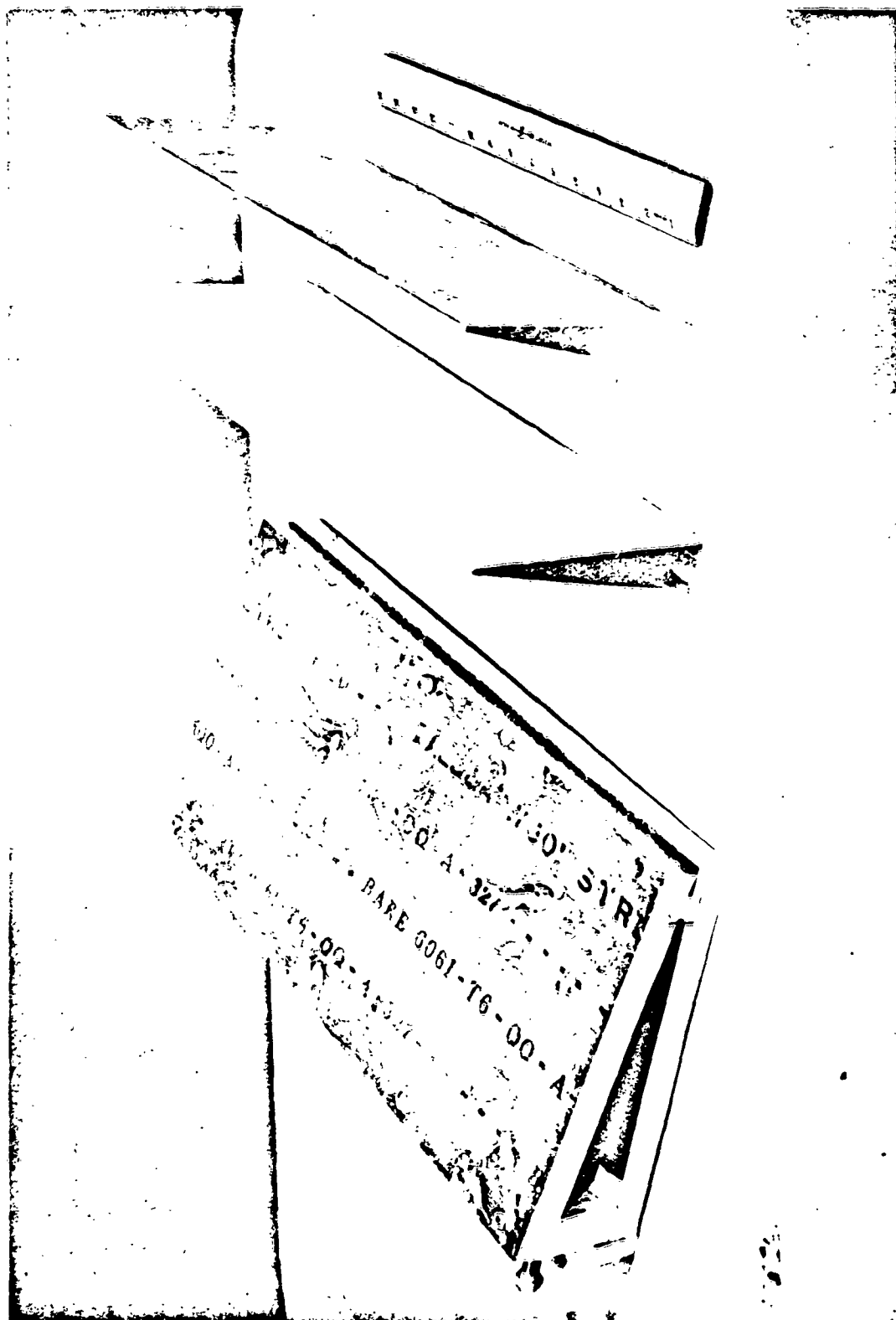


Figure 4
MOLD FOR REINFORCED CERAMIC AIR FOIL

VIII pp 41-43)

Aluminum phosphate cement bonded, woven fiber reinforced, laminate structures can be fabricated with a negligible mold cost. A crude two foot long nose cone was made on a reinforced plastic mold using the wet lay up technique. After drying at 80 C for 1 week it was removed from the mold and free-fired at 300 C without loss of shape. A similarly fabricated 12" X 12" X 0.03" corrugated panel was also successfully formed. These large ceramic laminate structures display a surprising amount of flexibility and appear to have considerable impact resistance. (See Report III pp 40-43) The same technique was used in forming several air foil sections. Here, a more sophisticated mold assembly was employed in order to provide the smooth surfaces shown in Fig. 4. (See Report VIII pp 47-49)

PHYSICAL PROPERTIES OF SiO_2 FIBER REINFORCED ALUMINUM PHOSPHATE BONDED LAMINATES

FLEXURAL STRENGTH AND ELASTIC MODULUS

Throughout the course of the project particular emphasis was placed on the development of a strong laminate. The results from flexural strength tests, made at room temperature, and at elevated temperatures, were largely relied upon to indicate the relative worth of the various experimental bonding cements. Representative values are shown in Tables III and VI where it may be noted that the strongest filament wound laminates developed so far had strengths of approximately 20,000 psi at room temperature and 24,000 psi when measured at 500 C. By pre-tensioning the reinforcing fiber during laminate fabrication, strengths as high as 29,000 psi were obtained on samples measured at room temperature after curing at 300 C. Such laminates showed 24,000 psi strength at 500 C. These flexural strength tests were performed in accordance with the ASTM 3-point bending test using a 1" X 4" X 1/8" specimen.

Although results from these tests were useful in providing comparative data, the actual strength of such laminates should be determined from tests more nearly simulating conditions that would be encountered in use, particularly with respect to the mode of stress application. A preliminary study was made to show what, if any, strength difference would be found when testing a standard laminate sample by pure bending instead of by 3-point loading. The average of results obtained at room temperature on eleven identically fabricated samples (150 4/3 SiO_2 yarn bonded with cement Formulation 3) were:

	<u>3-point bending</u>	<u>pure bending</u>
Flexural strength (psi)	12,600	9,200
Elastic modulus (psi)	2.64×10^6	3.19×10^6

TABLE V
FLEXURAL STRENGTH AND ELASTIC MODULI OF SEVERAL
CEMENT BONDED LAMINATES

LAMINATE*	<u>A</u>		<u>B</u>		<u>C</u>	
<u>TEST TEMPERATURE</u>	<u>r.t.</u>	<u>500 C</u>	<u>r.t.</u>	<u>500 C</u>	<u>r.t.</u>	<u>500 C</u>
Flexural strength (psi)	15,900	10,700 ^a	19,900	13,700	17,500	18,400
Corrected deflection (in)	0.028	0.016	0.032	0.026	0.028	0.025
Elastic modulus (psi)10 ⁶	3.7	3.2	3.4	3.6	3.8	4.0

* All laminates were filament wound and cured at 300 C before testing.
For cement compositions see Table III.

LAMINATE A: 12 end fused SiO₂ roving bonded with Formulation 3 cement.
Values shown are average of 2 results. a)(Samples tested at 500 C were of inferior quality.)

LAMINATE B: 150 4/3 fused SiO₂ yarn bonded with Formulation 3-3M cement.
Values shown are average of 3 results.

LAMINATE C: 150 4/3 fused SiO₂ yarn bonded with Formulation 3-3S cement.
Values shown are average of 3 results.

These observed differences due to testing method are in accordance with results reported in the literature for reinforced plastic laminates. The difference is considered as basically due to shear deformation, local interlaminar shear failures and the effect of the loading nose (in 3-point bending) in holding down a buckling surface. (See Report VII pp 42-47)

Elastic modulus values, calculated from corrected deflection data, were obtained along with flexural strength (3-point bending) at room temperature and at 500 C for several samples. Corrections in sample deflection (which was obtained from motion of the cross-head during loading) were made to eliminate errors introduced by "stretch" in the test system and crushing of the sample face in contact with the loading nose. As shown in Table V, deflection (a measure of sample extensibility) generally correlated with flexural strength.

IMPACT STRENGTH

The aluminum phosphate cement bonded fiber reinforced laminates, after curing at 300 C, seemed tougher and less notch sensitive than unreinforced ceramic bodies. Samples broken in flexure frequently appeared to be unharmed because the reinforcing fibers remained intact even though the cementing bond had fractured. An attempt to measure the impact strength of such laminates by the Izod impact test method failed. The notched specimens did not sever cleanly in the fixture, and did not break where notched. The unsevered portion created a variable energy absorbing drag on the impact hammer so that meaningful impact data could not be obtained. The test did demonstrate the non-ceramic-like properties of the cement bonded laminates. (See Report VIII pp 24-26)

MOISTURE ABSORPTION

The true specific gravities of the materials used in the laminates fall in the 2.2-2.5 gm/cc range. Since bulk specific gravity of the laminate

samples usually ranged from 1.6 to 1.8 gm/cc, the laminates obviously contained from 25 - 30% voids.

A silica roving reinforced laminate sample bonded with cement Formulation 3-6A had 12.4% water absorption, as measured by weight increase after 24 hours immersion in water at 20 C (ASTM manual standards on plastics p 482). The original sample weight was restored by heating at 125 C. No strength tests were made on the sample, but water immersion and subsequent drying appeared to have no detrimental effect. Partial reduction of water absorption (to 8.6%) was accomplished by impregnating the cured sample with a suspension of colloidal SiO_2 containing approximately 30% solids. More effective methods for sealing the laminate surface to prevent moisture pick-up remain to be developed. (See Report VIII pp 25-28)

THERMAL SHOCK RESISTANCE

None of the laminate samples appeared to have suffered from thermal shock as a result of rapid cooling in air from temperatures of 500-700 C. One set of Formulation 3-6A bonded samples was given a more severe test by quenching in cold water from 500 C. No cracking, spalling, or other indication of change in the laminate could be detected by visual inspection even when the test was repeated. (See Report VIII pp 28-29)

ELECTRICAL PROPERTIES

Filament wound laminates (fabricated with 12 end SiO_2 roving bonded with cement Formulations 3-3A or 3-3A3M) cured at 300 C were tested to determine electrical properties at room temperature and at 500 C. Electrical effects due to moisture adsorption from a 50% RH atmosphere were also noted. These tests were made at a frequency of one megacycle/sec. Wave guide tests, to determine dielectric constant and loss tangent at 9,150 megacycles/sec, were made during heating and cooling (20 C to 593 C) on SiO_2 reinforced laminates

bonded with cement Formulation 3 or 3-6A, machined to size after curing at 300 C. Sample dimension and weight before and after testing were determined and electrical effects due to sample thickness, moisture absorption, and measurement time, were noted. The laminate specimens were oriented in the wave guide with their grain perpendicular to the electric field polarization. Corrections for sample clearance in the wave guide were included in the dielectric calculations.

During testing, the samples were held at a given temperature for from 1/2 to 1 hour. The time at temperature apparently had relatively little effect on the test results. The material was essentially unchanged by the temperature cycling, no density or dimensional changes could be detected. Water absorption (18% due to soaking the specimen for 24 hours in water) significantly raised the dielectric constant and loss tangent but the effect was essentially reversible on drying at 135 C. As shown in Table VI, initially dry samples measured at 9,150 M/sec had remarkably stable dielectric constant values of approximately 3.0 and loss tangent values between 0.010 and 0.015 over the temperature range from 20 to 593 C. Samples measured at 1 M/sec. show less uniformity, having dielectric constant values for approximately 3.0 at room temperature, increasing to about 4.0 at 500 C while power factor values range from 0.01 at room temperature to 0.10 and higher at 500 C.

TABLE VI
SUMMARY OF PHYSICAL AND ELECTRICAL PROPERTIES OF
SOME INORGANIC LAMINATES

LAMINATE DESCRIPTION

Reinforcement: continuous filament fused SiO_2 (2400 strand, starch-oil coated) in the form of 150 4/3 yarn or 12 end roving as indicated.

Matrix: Aluminum phosphate bonded cement, Formulation 3 and variations as shown.

Fabrication: Test specimens filament wound on laminating mandrel from reinforcement strands passed through slurry of bonding cement. Dried at 80 C for 7 days and at 150 C for 3 days in mold. Free-fired (cured) for 1/2 hour at 300 C.

GENERALLY APPLICABLE PROPERTIES

Apparent specific gravity: 1.6 to 1.8

Voids: (calculated from approximate specific gravity) 25 to 30%

Water absorption: 12 to 18%, absorbed water readily removed by drying. Physical characteristics of bonding cement appeared unchanged by 24 hour immersion in water.

Temperature stability: No measurable change in size or weight of cured laminate after heating at 590 C. Flexural strength at temperature gradually decreased with long term heating at 500 C and above. Flexural strength at room temperature much reduced by prior heating at 500 C.

Thermal shock resistance: No visible damage when quenched in air from 700 C, or when quenched in cold water from 500 C (no higher temperatures were tried).

Impact strength: Laminates cured at 300 C are not severed when broken and show little if any notch sensitivity.

TABLE VI (cont.)

PROPERTY	TEST TEMPERATURE			Reference Report, page
	r.t.	500 C	r.t. From 500 C	
<u>Form. 3 bonded yarn</u>				
Flexural strength (psi)	15,300	18,200	4,600	VII 19a, 25
<u>Form. 3 bonded roving</u>				
Flexural strength (psi)	16,000	14,400		VI 25a
Elastic modulus $\times 10^6$	3.7	3.2		VI 30a
Diel. Const. at 9,150 M/sec	2.8	3.1	2.8	VIII 35
Power factor at 9,150 M/sec	0.012	0.012	0.012	VIII 38
<u>Form. 3-3A bonded yarn</u>				
Flexural strength (psi)	19,900	13,700		VII 19a
Elastic modulus $\times 10^6$	3.4	3.6		VI 30a
<u>Form. 3-3A bonded roving</u>				
Flexural strength (psi)	15,400	15,200		VII 19a
Diel. Const. at 1 M/sec	3.2	4.2	2.9	VII 40a
Power factor at 1 M/sec	0.037	0.125	0.009	VII 40a
DC vol. resistivity (ohm-cm) 10^8	1.3	1.6	1.3	VII 40a
<u>Form. 3-6A bonded yarn</u>				
Flexural strength (psi)	19,100	24,000		VII 19a
<u>Form. 3-6A bonded roving</u>				
Flexural strength (psi)	21,400	20,700		VII 19a
Diel. const. at 9,150 M/sec	3.0	2.9	2.8	VIII 35
Power factor at 9,150 M/sec	0.05	0.05	0.014	VIII 35

STATUS OF INORGANIC CEMENT BONDED LAMINATES

In summary: let us briefly review the results obtained from fused SiO_2 fiber reinforced laminates bonded with aluminum phosphate type cements; list the mechanisms that we believe may be active in governing the flexural strengths observed; and suggest means for improving the strength of such laminates.

RESULTS

1. Cement Formulation 3 bonded laminates had fairly good room temperature flexural strength after having been heated at 300 C (15,000 psi) and even better strength if tested at 500 C after 1/2 hour at temperature (18,000 psi). Strength at temperature was diminished by extended heating at 600 C or higher (9,000 psi). If tested at room temperature, after having been heated at 500 C, the laminates were relatively weak (4,600 psi).

2. When short fibers were used as a portion of the filler content in cement Formulation 3, an appreciable improvement in laminate strength was observed. Best results were obtained with asbestos-containing cement Formulation 3-6A which produced laminates having 19,000 psi room temperature flexural strength after heating at 300 C and 24,000 psi flexural strength at 500 C.

3. Laminates bonded with poorly proportioned cements employing a pre-reacted magnesium-aluminum phosphate adhesive phase, though much lower in strength than the others, maintained a high percentage of their flexural strength when measured at room temperature after having been heated at 500 C. For example: laminates bonded with cement formulation MA-3P had room temperature flexural strengths of 6,300 psi after heating at 300 C; 5,300 psi after heating at 500 C; and 8,700 psi when measured at 500 C.

MECHANISMS EFFECTING LAMINATE STRENGTH

1. In a fiber reinforced laminate structure with the cement under a compressive stress, the reinforcement assumes the total test load until extension of the fibers removes the compressive stress on the cement. Further loading.

is then shared by fiber and cement until the elastic limit of the cement is exceeded. If the cement is brittle, and well bonded to the fiber reinforcement, the fracture in the cement is propagated, causing failure of the entire structure. If the tightly bonded fiber is brittle at the test temperature the laminate will break. If the fiber reinforcement is either flexible or not tightly bonded the laminate sample will appear unbroken, being held together by the nearly intact reinforcing fibers. Therefore, the load which the laminate structure can support at a given temperature depends on three factors: (a) the compressive stress on the cement to be overcome by loading and extension of the reinforcing fibers, (b) the elastic moduli of the cement and of the reinforcing fibers at the test temperature, and (c) the extensibility of the cement.

2. Any degradation of the reinforcing fiber reduces the effective load that the reinforcement can support by reducing the load bearing cross section. Abrasion of fiber surface, spalling which may result from surface devitrification, or chemical reaction with the cement bond, all serve to reduce the effective strength of the reinforcing fibers.

3. The strength of the cement bond, and possibly its effective extensibility, depend on the strength of the adhesive phase holding the filler particles together, on the effective packing density of the cement composite, and on the shape and size of the filler materials used.

MEANS FOR FUTURE IMPROVEMENT OF LAMINATE STRENGTH

1. At present fused SiO_2 continuous filament yarns, etc., appear to be the only available high temperature, high strength, material for laminate reinforcement. But SiO_2 fibers are inadequate for maintaining laminate strength during long term exposure to elevated temperatures. To meet this need, a reinforcing fiber having a higher elastic modulus at high temperature (i.e., a

higher annealing temperature) must be discovered or developed.

2. Obviously, in order to realize the inherent strength of the fiber reinforcement, physical damage must be prevented not only during laminate fabrication but also during the curing cycle and at use temperatures. Such damage can be reduced or prevented in several ways:

- a) Pre-coat individual fibers with a thin protective film that is non-soluble in acidic solutions, preferably a metallo-organic compound that deposits a soft ash when pyrolyzed. (Metal stearates modified to make them less hydrophobic should be tried. Silane coating appears to do a good job on "E" glass, and might be used to advantage on fused SiO_2 fibers.)
- b) Use cement fillers that are less abrasive in nature, choose minerals that are softer than the reinforcing fiber (i.e., substitute calcined $\text{Al}(\text{OH})_3$ for fused Al_2O_3), employ particulate fillers with finer grain size (500 mesh or smaller). Use temperature-stable, chemically inert, minerals having fibrous or needle-shaped particles (polygorskite is of particular interest).
- c) Avoid corrosive chemical attack of the fiber reinforcement by eliminating unreacted H_3PO_4 in the cement (use a pre-reacted adhesive solution). Reduce the acidity of the adhesive solution by making additions of magnesia, etc. Provide particulate fillers in the cement that form stable phosphates at low temperatures (Fe_2O_3 is a case in point). Make every effort to protect the SiO_2 fiber from contact with alkali ions that promote devitrification (the alkali-contaminated starch-oil coating must go).

3. Increase the strength of the cement by:

- a) Improving the strength of the adhesive phase (assuring maximum development of $\text{Al}(\text{H}_2\text{PO}_4)_3$ or related compositions by pre-reacting to achieve complete solution).
- b) Further investigate the possibility of obtaining lower hydrates that are

soluble but which form bonds comparable to aluminum phosphate in strength (the magnesium aluminum phosphate bond MA-3P for example).

- c) Provide particulate fillers that will form strong, temperature stable, chemical bonds with the aluminum phosphate adhesive phase at slightly elevated temperatures so that cement strength is developed with low temperature curing (calcined $\text{Al}(\text{OH})_3$, Fe_2O_3 , etc.)
- d) Adjust the adhesive to filler ratio for development of maximum strength with the particular reinforcement used (yarn reinforcement robs cement of the soluble adhesive phase which is drained to the interior of the fiber bundle).
- e) Establish a time-temperature curing cycle that will prevent micro-bubbling (during dehydration of the aluminum phosphate bond) and promote the development of strong crystals in the bonding phase.
- f) Achieve the best fired cement density possible through using proper particle size distribution in the cement filler.
- g) Eliminate tensile stress on the cement by altering the cement composition to provide thermal expansion characteristics more nearly matching those of the reinforcing fiber.

4. Increase the effective extensibility of the cement by:

- a) Employing micro-fibers as a portion of the cement filler material.
- b) Developing a non-brittle, probably non-crystalline, adhesive phase.

5. Increase the compressive stress on the cement in the laminate structure by pre-stressing the fiber reinforcement in tension. With the present fused SiO_2 fiber reinforcement this means for improving laminate strength is limited in its application to structures that either never are heated in the annealing range of fused SiO_2 , or are held only briefly in this range and not expected to retain their strength when cooled from the high temperature. Pre-stressing cannot be of value in improving strength of laminates intended for

long term use at high temperature until a non-brittle high modulus, high annealing range, reinforcing fiber is developed.

Of all of these suggested improvements, the two that would make outstanding contributions to the advancement of inorganic laminate technology are: achieving a notable increase in the elastic modulus of the continuous filament reinforcing fiber; and producing a binder capable of greater extension before rupture. These are fundamental necessities. Neither are likely to be accomplished easily, but concentrated effort should be directed toward their realization.